

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
2 October 2003 (02.10.2003)

PCT

(10) International Publication Number  
**WO 03/081702 A2**

(51) International Patent Classification<sup>7</sup>: **H01M 4/92**,  
B01J 23/42, 23/46, 23/56, 23/652, 23/62, 23/72, 23/89,  
C22C 5/04

(21) International Application Number: PCT/US03/08852

(22) International Filing Date: 21 March 2003 (21.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/366,519 21 March 2002 (21.03.2002) US

(71) Applicants (for all designated States except US): **SYMYX TECHNOLOGIES, INC.** [US/US]; 3100 Central Expressway, Santa Clara, CA 95051 (US). **HONDA GIKEN KOGYO KABUSHIKI KAISHA** [JP/JP]; c/o Kabushiki Kaisha Honda, Gijyutsu Kenkyusho, 4-1, Chuo-1-chome, Wako-shi, Saitama 351-0193 (JP).

(72) Inventors; and

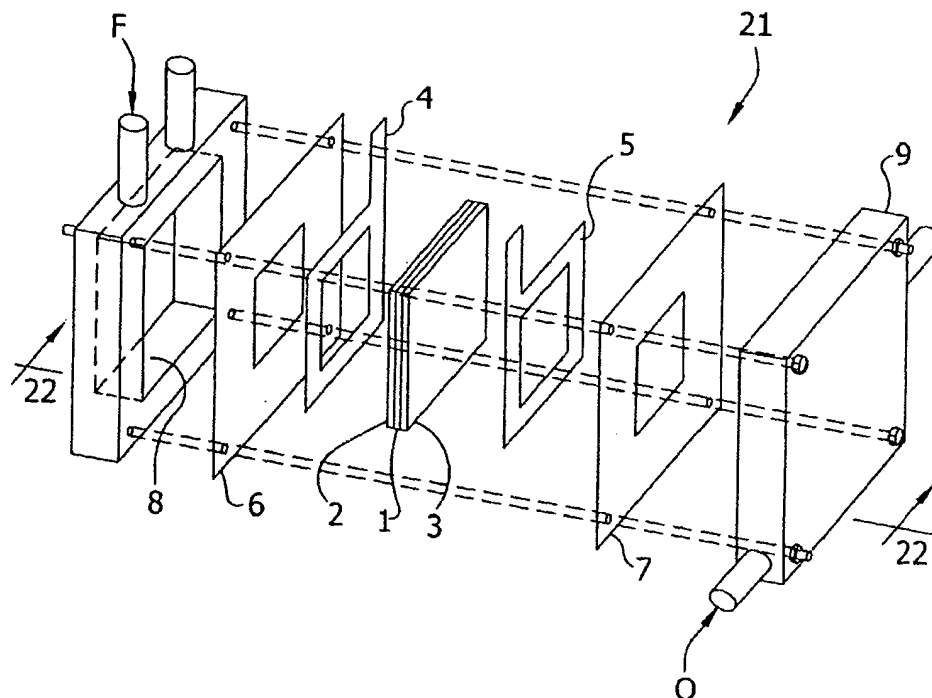
(75) Inventors/Applicants (for US only): **STRASSER, Peter** [DE/US]; 551 Mariposa Avenue, Apt. 7, Mountain View, CA 94041 (US). **GORER, Alexander** [IL/US]; 455 Mill

River Lane, San Jose, CA 95134 (US). **DEVENNEY, Martin** [IE/US]; 1311 Bonita Avenue, Mountain View, CA 94040 (US). **FAN, Qun** [US/US]; 1178 Quintana Way, Fremont, CA 94539 (US). **CHONDROUDIS, Konstantinos** [GR/US]; 542 Firloch Avenue, Apt. #3, Sunnyvale, CA 94086 (US). **GIAQUINTA, Daniel, M.** [US/US]; 149 Jasmine Court, Mountain View, CA 94043 (US). **HE, Ting** [CN/US]; 5794 Norn Street, Dublin, OH 43016 (US). **OYANAGI, Hiroyuki** [JP/JP]; c/o Kabushiki Kaisha Honda, Gijyutsu Kenkyusho, 4-1, Chuo-1-chome, Wako-shi, Saitama 351-0193 (JP). **URATA, Kenta** [JP/JP]; c/o Kabushiki Kaisha Honda, Gijyutsu Kenkyusho, 4-1, Chuo-1-chome, Wako-shi, Saitama 351-0193 (JP). **IWASAKI, Kazuhiko** [JP/JP]; c/o Kabushiki Kaisha Honda, Gijyutsu Kenkyusho, 4-1, Chuo-1-chome, Wako-shi, Saitama 351-0193 (JP). **FUKUDA, Hiroichi** [JP/JP]; c/o Kabushiki Kaisha Honda, Gijyutsu Kenkyusho, 4-1, Chuo-1-chome, Wako-shi, Saitama 351-0193 (JP).

(74) Agents: **RITCHEY, Steven, M.** et al.; Senniger, Powers, Leavitt & Roedel, 1 Metropolitan Square, 16th Floor, St. Louis, MO 63102 (US).

[Continued on next page]

(54) Title: FUEL CELL CATALYST OF Pt-Rh-W/Sn/Cu/Mo



(57) Abstract: An improved fuel cell catalyst containing platinum, rhodium at least one of tungsten, tin, and copper, and optionally molybdenum, in metallic oxidation states. Additionally, the platinum and rhodium are at concentrations such that the sum of their concentrations is no greater than 85 atomic percent.

BEST AVAILABLE COPY

WO 03/081702 A2



(81) **Designated States (national):** AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— without international search report and to be republished upon receipt of that report

(84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

## FUEL CELL CATALYST OF Pt-Rh-W/Sn/Cu/Mo

### BACKGROUND OF THE INVENTION

#### Field of The Invention

5       The present invention relates to metal catalysts, especially to catalysts which comprise platinum, rhodium, at least one of tungsten, tin, and copper, and optionally molybdenum, which are useful in fuel cell electrodes and other catalytic structures.

#### Background Information

10       A fuel cell is an electrochemical device for directly converting the chemical energy generated from an oxidation-reduction reaction of a fuel such as hydrogen or hydrocarbon-based fuels and an oxidizer such as oxygen gas (in air) supplied thereto into a low-voltage direct current. Thus, fuel cells chemically combine the molecules of a fuel and an oxidizer without burning, dispensing with the inefficiencies and pollution of traditional combustion.

15       A fuel cell is generally comprised of a fuel electrode (anode), an oxidizer electrode (cathode), an electrolyte interposed between the electrodes (alkaline or acidic), and means for separately supplying a stream of fuel and a stream of oxidizer to the anode and the cathode, respectively. In operation, fuel supplied to the anode is oxidized, releasing electrons which are conducted via an external circuit to the  
20       cathode. At the cathode, the supplied electrons are consumed when the oxidizer is reduced. The current flowing through the external circuit can be made to do useful work.

      There are several types of fuel cells, including those having electrolytes of: phosphoric acid, molten carbonate, solid oxide, potassium hydroxide, and proton  
25       exchange membrane. A phosphoric acid fuel cell operates at about 160-220 °C, and preferably at about 190-200 °C. This type of fuel cell is currently being used for multi-megawatt utility power generation and for co-generation systems (i.e., combined heat and power generation) in the 50 to several hundred kilowatts range.

      In contrast, proton exchange membrane fuel cells use a solid proton-  
30       conducting polymer membrane as the electrolyte. Typically, the polymer membrane is maintained in a hydrated form during operation in order to prevent loss of ionic conduction which limits the operation temperature typically to between about 70 and about 120 °C depending on the operating pressure, and preferably below about 100 °C. Proton exchange membrane fuel cells have a much higher power density than  
35       liquid electrolyte fuel cells (e.g., phosphoric acid), and can vary output quickly to meet shifts in power demand. Thus, they are suited for applications such as in automobiles and small scale residential power generation where quick startup is a consideration.

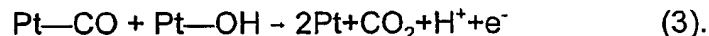
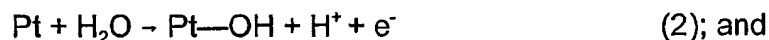
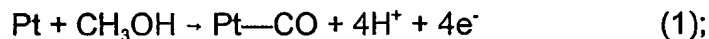
In some applications (e.g., automotive) pure hydrogen gas is the optimum fuel; however, in other applications where a lower operational cost is desirable, a reformed hydrogen-containing gas is an appropriate fuel. A reformed-hydrogen containing gas is produced, for example, by steam-reforming methanol and water at 200-300 °C to a hydrogen-rich fuel gas containing carbon dioxide. Theoretically, the reformat gas consists of 75 vol% hydrogen and 25 vol% carbon dioxide. In practice, however, this gas also contains nitrogen, oxygen, and, depending on the degree of purity, varying amounts of carbon monoxide (up to 1 vol%). Although some electronic devices also reform liquid fuel to hydrogen, in some applications the conversion of a liquid fuel directly into electricity is desirable, as then a high storage density and system simplicity are combined. In particular, methanol is an especially desirable fuel because it has a high energy density, a low cost, and is produced from renewable resources.

For the oxidation and reduction reactions in a fuel cell to proceed at useful rates, especially at operating temperatures below about 300 °C, electrocatalyst materials are typically provided at the electrodes. Initially, fuel cells used electrocatalysts made of a single metal, usually platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), osmium (Os), silver (Ag) or gold (Au) because they are able to withstand the corrosive environment - platinum being the most efficient and stable single-metal electrocatalyst for fuel cells operating below about 300 °C. While these elements were first used in fuel cells in metallic powder form, later techniques were developed to disperse these metals over the surface of electrically conductive supports (e.g., carbon black) to increase the surface area of the electrocatalyst which in turn increased the number of reactive sites leading to improved efficiency of the cell. Nevertheless, fuel cell performance typically declines over time because the presence of electrolyte, high temperatures and molecular oxygen dissolve the electrocatalyst and/or sinter the dispersed electrocatalyst by surface migration or dissolution/re-precipitation.

Although platinum is the most efficient and stable single-metal electrocatalyst for fuel cells, it is costly and an increase in electrocatalyst activity over platinum is necessary for wide scale commercialization of fuel cell technology. The development of cathode fuel cell electrocatalyst materials faces longstanding challenges. The greatest challenge is the improvement of the electrode kinetics of the oxygen reduction reaction. In fact, sluggish electrochemical reaction kinetics have prevented attaining the thermodynamic reversible electrode potential for oxygen reduction. This is reflected in exchange current densities of around  $10^{-10}$  to  $10^{-12}$  A/cm<sup>2</sup> for oxygen reduction on, for example, Pt at low and medium temperatures. A factor contributing to this phenomenon includes the fact that the desired reduction of oxygen to water is a four-electron transfer reaction and typically involves breaking a strong O-O bond early in the reaction. In addition, the open

circuit voltage is lowered from the thermodynamic potential for oxygen reduction due to the formation of peroxide and possible platinum oxides which inhibit the reaction. A second challenge is the stability of the oxygen electrode (cathode) during long-term operation. Specifically, a fuel cell cathode operates in a regime in which even the most unreactive metals are not completely stable. Thus, alloy compositions which contain non-noble metal elements may have a rate of corrosion which would negatively impact the projected lifetime of a fuel cell. The corrosion may be more severe when the cell is operating near open circuit conditions (which is the most desirable potential for thermodynamic efficiency).

Electrocatalyst materials at the anode also face challenges during fuel cell operation. Specifically, as the concentration of carbon monoxide (CO) rises above about 10 ppm in the fuel the surface of the electrocatalyst can be rapidly poisoned. As a result, platinum (by itself) is a poor electrocatalyst if the fuel stream contains carbon monoxide (e.g., reformed-hydrogen gas typically exceeds 100 ppm). Liquid hydrocarbon-based fuels (e.g., methanol) present an even greater poisoning problem. Specifically, the surface of the platinum becomes blocked with the adsorbed intermediate, carbon monoxide (CO). It has been reported that H<sub>2</sub>O plays a key role in the removal of such poisoning species in accordance with the following reactions:



As indicated by the foregoing reactions, the methanol is adsorbed and partially oxidized by platinum on the surface of the electrode (1). Adsorbed OH, from the hydrolysis of water, reacts with the adsorbed CO to produce carbon dioxide and a proton (2,3). However, platinum does not form OH species well at the potentials fuel cell electrodes operate (e.g., 200 mV-1.5 V). As a result, step (3) is the slowest step in the sequence, limiting the rate of CO removal, thereby allowing poisoning of the electrocatalyst to occur. This applies in particular to a proton exchange membrane fuel cell which is especially sensitive to CO poisoning because of its low operating temperatures.

One technique for increasing electrocatalytic cathodic activity during the reduction of oxygen and electrocatalytic anodic activity during the oxidation of hydrogen is to employ an electrocatalyst which is more active, corrosion resistant, and/or more poison tolerant. For example, increased tolerance to CO has been reported by alloying platinum and ruthenium at a 50:50 atomic ratio (see, D. Chu and S. Gillman, J. Electrochem. Soc. 1996, 143, 1685). The electrocatalysts proposed to date, however, leave room for further improvement.

## BRIEF SUMMARY OF THE INVENTION

Briefly, therefore, the present invention is directed to a catalyst for use in oxidation or reduction reactions, the catalyst comprising platinum, rhodium, at least one of tungsten, tin, and copper, and optionally molybdenum, in metallic oxidation states, provided the platinum and rhodium are at concentrations such that the sum of said concentrations is no greater than about 85 atomic percent.

The present invention is also directed to a supported electrocatalyst powder for use in electrochemical reactor devices, the supported electrocatalyst powder comprising a catalyst comprising platinum, rhodium, at least one of tungsten, tin, and copper, and optionally molybdenum, in metallic oxidation states, provided the platinum and rhodium are at concentrations such that the sum of said concentrations is no greater than about 85 atomic percent, and electrically conductive support particles upon which the catalyst is dispersed.

The present invention is also directed to a fuel cell electrode, the fuel cell electrode comprising electrocatalyst particles and an electrode substrate upon which the electrocatalyst particles are deposited, the electrocatalyst particles comprising a catalyst comprising platinum, rhodium, at least one of tungsten, tin, and copper, and optionally molybdenum, in metallic oxidation states, provided the platinum and rhodium are at concentrations such that the sum of said concentrations is no greater than about 85 atomic percent.

The present invention is also directed to a fuel cell comprising an anode, a cathode, a proton exchange membrane between the anode and the cathode, and a catalyst comprising platinum, rhodium, at least one of tungsten, tin, and copper, and optionally molybdenum, in metallic oxidation states, provided the platinum and rhodium are at concentrations such that the sum of said concentrations is no greater than about 85 atomic percent for the catalytic oxidation of a hydrogen-containing fuel or the catalytic reduction of oxygen.

The present invention is also directed to a method for the electrochemical conversion of a hydrogen-containing fuel and oxygen to reaction products and electricity in a fuel cell comprising an anode, a cathode, a proton exchange membrane therebetween, a catalyst comprising platinum, rhodium, at least one of tungsten, tin, and copper, and optionally molybdenum, in metallic oxidation states, provided the platinum and rhodium are at concentrations such that the sum of said concentrations is no greater than about 85 atomic percent, and an electrically conductive external circuit connecting the anode and cathode, the method comprising contacting the hydrogen-containing fuel or the oxygen and the catalyst to catalytically oxidize the hydrogen-containing fuel or catalytically reduce the oxygen.

The present invention is also directed to an unsupported catalyst layer on a surface of a electrolyte membrane or an electrode, said unsupported catalyst layer comprising platinum, rhodium, at least one of tungsten, tin, and copper, and

optionally molybdenum, in metallic oxidation states, provided the platinum and rhodium are at concentrations such that the sum of said concentrations is no greater than about 85 atomic percent.

5 The foregoing and other features and advantages of the present invention will become more apparent from the following description and accompanying figures.

#### BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

FIG. 1 is a schematic structural view showing essential members of a fuel cell.

FIG. 2 is a side view of a fuel cell.

10 FIG. 3 is a photograph of an electrode array comprising thin-film alloy compositions deposited on individually addressable electrodes.

#### DETAILED DESCRIPTION OF THE INVENTION

15 The present invention is directed to a metal-containing substance having electrocatalytic activity for use in, for example, fuel cells (e.g., an electrocatalyst). In one embodiment the metal-containing substance is an alloy of the components. However, it is to be noted that the substance (e.g., electrocatalyst) may be a mixture of discrete amounts of the components (e.g., a mixture of metal powders or a mixture of deposits), wherein a discrete amount of the components may comprise a single component or a combination of components (e.g., an alloy).

20 In general, it is desirable to decrease the concentration of noble metals (especially platinum) to reduce the cost of an electrocatalyst. However, as the concentrations of noble metals are decreased, the electrocatalyst may become more susceptible to corrosion, and/or the activity may be diminished. Thus, it is desirable to achieve the most activity per weight percent of noble metals without  
25 compromising, for example, the life cycle of the fuel cell in which the electrocatalyst is placed (see, end current density / weight fraction of platinum as set forth in Tables A and B, infra). Additionally, the composition of the present invention is preferably optimized to limit noble metal concentration while improving corrosion resistance and/or activity, as compared to platinum.

30 The present invention is thus directed to a metal-containing substance (e.g., catalyst or alloy) that comprises platinum, rhodium, at least one of tungsten, tin, and copper, and optionally molybdenum. Furthermore, the foregoing elements, when present in the catalyst, are substantially in their metallic oxidation states. Stated another way, the average oxidation states of the foregoing catalyst elements are at  
35 or near zero. Although there may be portions of the catalyst wherein the oxidation states of one or more of these elements is greater than the zero, the average oxidation state of each of these elements throughout the entire catalyst is less than the lowest commonly occurring oxidation state for that particular element (e.g., the

lowest commonly occurring oxidation state for platinum, rhodium, tungsten, tin, and molybdenum is 2 and for copper it is 1). Therefore, in several embodiments of the present invention, the average oxidation states of the foregoing elements, when present in the catalyst, are less than 1, 0.5, 0.1, or 0.01, and may be zero.

5       The catalyst of the present invention comprises amounts of platinum, rhodium, and at least one of tungsten, tin, and copper, and optionally molybdenum which are sufficient for the metals, present therein, to play a role in the catalytic activity and/or crystallographic structure of, for example, the alloy. Stated another way, the concentrations of platinum, rhodium, and at least one of tungsten, tin, and  
10       copper, and optionally molybdenum are such that the presence of the metals would not be considered an impurity. For example, when present, the concentrations of each of platinum, rhodium, tungsten, tin, copper and/or molybdenum are at least about 0.1, 0.5, 1, or even 5 atomic percent. Additionally, the concentrations of platinum and rhodium are controlled such that the sum of their concentrations is no  
15       greater than 85 atomic percent. In other embodiments the sum of their concentrations is no greater than about 80, 75, or even 70 atomic percent.

      In one embodiment the catalyst of the present invention comprises at least about 5 atomic percent of platinum. In another embodiment the concentration of platinum is at least about 10 atomic percent. In the foregoing or other embodiments  
20       the concentration of platinum is no more than 85 atomic percent. In another embodiment the concentration of platinum is no more than about 75 atomic percent. Accordingly, the concentration of platinum may, in some embodiments, be between about 5 and 85 atomic percent or between about 10 and about 75 atomic percent.

      In one embodiment the catalyst of the present invention comprises at least  
25       about 5 atomic percent of rhodium. In another embodiment the concentration of rhodium is at least about 10 atomic percent. In the foregoing or other embodiments the concentration of rhodium is no more than 85 atomic percent. In another embodiment the concentration of rhodium is no more than about 75 atomic percent. Accordingly, the concentration of rhodium may, in some embodiments, be between  
30       about 5 and 85 atomic percent or between about 10 and about 75 atomic percent.

      In one embodiment the catalyst of present invention comprises at least 15 atomic percent of tungsten, tin, copper, molybdenum, or a combination thereof. In another embodiment the concentration of one or more of these metals is at least about 20 atomic percent. In the foregoing or other embodiments the concentration  
35       of one or more of these metals may be no more than about 95, 90, 85, or 80 atomic percent (thus the sum of the concentrations of platinum and rhodium may be at least about 5, 10, 15, or 20 atomic percent). Accordingly, the concentration of tungsten, tin, copper, molybdenum, or a combination thereof may, in some embodiments, be between about 15 and about 90 atomic percent or between about 20 and about 80  
40       atomic percent.



In view of the foregoing, in one embodiment the catalyst comprises a concentration of platinum that is between about 5 and 85 atomic percent, a concentration of rhodium that is between about 5 and 85 atomic percent, and a concentration of tungsten, tin, copper, molybdenum, or a combination thereof that is between about 15 and about 90 atomic percent. In another embodiment the catalyst comprises a concentration of platinum that is between about 10 and about 75 atomic percent, a concentration of rhodium that is between about 10 and about 75 atomic percent, and a concentration of tungsten, tin, copper, molybdenum, or a combination thereof that is between about 20 and about 80 atomic percent.

In this regard it is to be noted that in one embodiment the substance of the present invention consists essentially of the foregoing metals (e.g., impurities that do not play a role in the catalytic activity and/or crystallographic structure of the catalyst may be present to some degree). However, in other embodiments it is possible that the substance may comprise other constituents as intentional additions. In view of the foregoing, the alloys of the present invention, while maintaining the same relative amounts of the constituents disclosed herein (i.e., platinum, rhodium, at least one of tungsten, tin, and copper, and optionally molybdenum), may comprise less than 100 percent of the disclosed atoms. Thus, in several embodiments of the present invention the total concentration of the disclosed atoms is greater than about 70, 80, 90, 95, or 99 atomic percent of the substance (e.g., electrocatalyst alloy).

#### Pt—Rh—W electrocatalysts

In accordance with one embodiment of the present invention, the catalyst comprises platinum, rhodium, and tungsten. In another embodiment the catalyst is an alloy that consists essentially of the platinum, rhodium, and tungsten.

In one Pt-Rh-W embodiment the concentration of each constituent metal may vary through a range. For example, in one embodiment the concentration of platinum is between about 5 and about 50 atomic percent. In another embodiment the concentration of platinum is between about 10 and about 45 atomic percent. In yet another embodiment the concentration of platinum is between about 15 and about 40 atomic percent. Similarly, the concentration of rhodium in one embodiment is between about 5 and about 50 atomic percent. In another embodiment the concentration of rhodium is between about 10 and about 40 atomic percent. In yet another embodiment the concentration of rhodium is between about 10 and about 30 atomic percent. The concentration of tungsten in one embodiment is between about 40 and about 85 atomic percent. In another embodiment the concentration of tungsten is between about 45 and about 80 atomic percent. In yet another embodiment the concentration of tungsten is between about 50 and about 70 atomic percent.

Additionally, it has been discovered that improved electrocatalytic activity (e.g., relative activity compared to platinum and/or activity per weight fraction of platinum) is achieved by controlling the relative concentrations of the various metals. For example, in one embodiment the concentration of platinum is between about 5 and about 50 atomic percent, the concentration of rhodium is between about 5 and about 50 atomic percent, and the concentration of tungsten is between about 40 and about 90 atomic percent. In another embodiment, the concentration of platinum is between about 10 and about 45 atomic percent, the concentration of rhodium is between about 10 and about 40 atomic percent, and the concentration of tungsten is between about 45 and about 80 atomic percent. In yet another embodiment the concentration of platinum is between about 15 and about 45 atomic percent, the concentration of rhodium is between about 10 and about 30 atomic percent, and the concentration of tungsten is between about 50 and about 70 atomic percent.

In a further embodiment the concentration of platinum is between about 10 and about 40 atomic percent, the concentration of rhodium is between about 5 and about 30 atomic percent, and the concentration of tungsten is between about 50 and about 70 atomic percent. In still another embodiment the concentration of platinum is between about 30 and about 40 atomic percent, the concentration of rhodium is between about 10 and about 20 atomic percent, and the concentration of tungsten is between about 50 and about 60 atomic percent.

#### Pt-Rh-Sn and Pt-Rh-Cu electrocatalysts

In accordance with one embodiment of the present invention, the catalyst comprises platinum, rhodium, and tin or copper. In another embodiment the catalyst is an alloy that consists essentially of the platinum, rhodium, and tin or copper.

In the Pt-Rh-Sn and Pt-Rh-Cu embodiments the concentration of each constituent metal may vary through a range. For example, in one embodiment the concentration of platinum is between about 10 and about 70 atomic percent. In another embodiment the concentration of platinum is between about 20 and about 60 atomic percent. Similarly, the concentration of rhodium in one embodiment is between about 10 and about 70 atomic percent. In another embodiment the concentration of rhodium is between about 20 and about 60 atomic percent. The concentration of tin or copper in one embodiment is between about 15 and about 70 atomic percent. In another embodiment the concentration of tin or copper is between about 20 and about 60 atomic percent.

Additionally, it has been discovered that improved electrocatalytic activity (e.g., relative activity compared to platinum and/or activity per weight fraction of platinum) is achieved by controlling the relative concentrations of the various metals. For example, in one embodiment the concentration of platinum is between about 10 and about 70 atomic percent, the concentration of rhodium is between about 10 and

about 70 atomic percent, and the concentration of tin or copper is between about 15 and about 70 atomic percent. In another embodiment, the concentration of platinum is between about 20 and about 60 atomic percent, the concentration of rhodium is between about 20 and about 60 atomic percent, and the concentration of tin or copper is between about 20 and about 60 atomic percent.

Pt-Rh-W-Sn, Pt-Rh-W-Mo, and Pt-Rh-W-Cu electrocatalysts

In accordance with one embodiment of the present invention, the catalyst comprises platinum, rhodium, tungsten, and tin, molybdenum, or copper. In another embodiment the catalyst is an alloy that consists essentially of the platinum, rhodium, tungsten, and tin, molybdenum, or copper.

In the Pt-Rh-W-Sn, Pt-Rh-W-Mo, and Pt-Rh-W-Cu embodiments the concentration of each constituent metal may vary through a range. For example, in one embodiment the concentration of platinum is between about 5 and about 70 atomic percent. In another embodiment the concentration of platinum is between about 10 and about 50 atomic percent. Similarly, the concentration of rhodium in one embodiment is between about 5 and about 70 atomic percent. In another embodiment the concentration of rhodium is between about 10 and about 50 atomic percent. The concentration of tungsten in one embodiment is between about 5 and about 70 atomic percent. In another embodiment the concentration of tungsten is between about 10 and about 50 atomic percent. The concentration of molybdenum, tin or copper in one embodiment is between about 5 and about 70 atomic percent. In another embodiment the concentration of tin, molybdenum, or copper is between about 10 and about 50 atomic percent.

Additionally, it has been discovered that improved electrocatalytic activity (e.g., relative activity compared to platinum and/or activity per weight fraction of platinum) is achieved by controlling the relative concentrations of the various metals. For example, in one embodiment the concentration of platinum is between about 5 and about 70 atomic percent, the concentration of rhodium is between about 5 and about 70 atomic percent, the concentration of tungsten is between about 5 and about 70 atomic percent, and the concentration of tin, molybdenum, or copper is between about 5 and about 70 atomic percent. In another embodiment, the concentration of platinum is between about 10 and about 50 atomic percent, the concentration of rhodium is between about 10 and about 50 atomic percent, the concentration of tungsten is between about 10 and about 50 atomic percent, and the concentration of tin, molybdenum, or copper is between about 10 and about 50 atomic percent.

In one Pt-Rh-W-Sn embodiment the concentration of platinum is between about 15 and about 25 atomic percent, the concentration of rhodium is between about 15 and about 25 atomic percent, the concentration of tungsten is between

about 15 and 45 atomic percent, and the concentration of tin is between about 15 and about 45 atomic percent.

Further, in one Pt-Rh-W-Mo embodiment the concentration of platinum is between about 15 and about 25 atomic percent, the concentration of rhodium is between about 15 and about 25 atomic percent, the concentration of tungsten is between about 15 and about 25 atomic percent, and the concentration of molybdenum is between about 35 and about 45 atomic percent.

In one Pt-Rh-W-Cu embodiment the concentration of platinum is between about 15 and about 25 atomic percent, the concentration of rhodium is between about 15 and about 25 atomic percent, the concentration of tungsten is between about 25 and 45 atomic percent, and the concentration of copper is between about 10 and about 40 atomic percent.

#### Pt-Rh-Sn-Cu electrocatalysts

In accordance with one embodiment of the present invention, the catalyst comprises platinum, rhodium, tin, and copper. In another embodiment the catalyst is an alloy that consists essentially of the platinum, rhodium, tin, and copper.

It has been discovered that improved electrocatalytic activity (e.g., relative activity compared to platinum and/or activity per weight fraction of platinum) is achieved by controlling the relative concentrations of the various metals. In several Pt-Rh-Sn-Cu embodiments the concentrations of platinum, rhodium, tin, and copper correspond to the concentrations of platinum, rhodium, and at least one tungsten, tin, copper, and optionally molybdenum set forth herein. Additionally, in one embodiment the concentration of platinum is between about 10 and about 25 atomic percent, the concentration of rhodium is between about 25 and about 40 atomic percent, the concentration of tin is between about 10 and about 25 atomic percent, and the concentration of copper is between about 25 and about 40 atomic percent.

#### Pt-Rh-Sn-Mo electrocatalysts

In accordance with one embodiment of the present invention, the catalyst comprises platinum, rhodium, tin, and molybdenum. In another embodiment the catalyst is an alloy that consists essentially of the platinum, rhodium, tin, and molybdenum.

In one Pt-Rh-Sn-Mo embodiment the concentration of each constituent metal may vary through a range. For example, in one embodiment the concentration of platinum is between about 10 and about 30 atomic percent. In another embodiment the concentration of platinum is between about 15 and about 25 atomic percent. Similarly, the concentration of rhodium in one embodiment is between about 10 and about 50 atomic percent. In another embodiment the concentration of rhodium is between about 15 and about 25 atomic percent. The concentration of tin in one

embodiment is between about 10 and about 30 atomic percent. In another embodiment the concentration of tin is between about 15 and about 25 atomic percent. The concentration of molybdenum in one embodiment is between about 10 and about 50 atomic percent. In another embodiment the concentration of molybdenum is between about 35 and about 45 atomic percent.

Additionally, it has been discovered that improved electrocatalytic activity (e.g., relative activity compared to platinum and/or activity per weight fraction of platinum) is achieved by controlling the relative concentrations of the various metals. For example, in one embodiment the concentration of platinum is between about 10 and about 30 atomic percent, the concentration of rhodium is between about 10 and about 50 atomic percent, the concentration of tin is between about 10 and about 30 atomic percent, and the concentration of molybdenum is between about 10 and about 50 atomic percent. In another embodiment, the concentration of platinum is between about 15 and about 25 atomic percent, the concentration of rhodium is between about 15 and about 25 atomic percent, the concentration of tin is between about 15 and about 25 atomic percent, and the concentration of molybdenum is between about 35 and about 45 atomic percent.

#### Pt-Rh-Cu-Mo electrocatalysts

In accordance with one embodiment of the present invention, the catalyst comprises platinum, rhodium, copper, and molybdenum. In another embodiment the catalyst is an alloy that consists essentially of the platinum, rhodium, copper, and molybdenum.

It has been discovered that improved electrocatalytic activity (e.g., relative activity compared to platinum and/or activity per weight fraction of platinum) is achieved by controlling the relative concentrations of the various metals. In several Pt-Rh-Cu-Mo embodiments the concentrations of platinum, rhodium, copper, and molybdenum correspond to the concentrations of platinum, rhodium, and at least one tungsten, tin, copper, and optionally molybdenum set forth herein. Additionally, in one embodiment the concentration of platinum is between about 30 and about 50 atomic percent, the concentration of rhodium is between about 10 and about 30 atomic percent, the concentration of copper is between about 10 and about 30 atomic percent, and the concentration of molybdenum is between about 10 and about 30 atomic percent.

#### Pt-Rh-Sn-Cu-Mo electrocatalysts

In accordance with one embodiment of the present invention, the catalyst comprises platinum, rhodium, tin, copper, and molybdenum. In another embodiment the catalyst is an alloy that consists essentially of the platinum, rhodium, tin, copper and molybdenum.

It has been discovered that improved electrocatalytic activity (e.g., relative activity compared to platinum and/or activity per weight fraction of platinum) is achieved by controlling the relative concentrations of the various metals. In several Pt-Rh-Sn-Cu-Mo embodiments the concentrations of platinum, rhodium, tin, copper, and molybdenum correspond to those concerning the concentrations of platinum, rhodium, and at least one tungsten, tin, copper, and optionally molybdenum set forth herein. Additionally, in one embodiment the concentration of platinum is between about 10 and about 30 atomic percent, the concentration of rhodium is between about 10 and about 30 atomic percent, the concentration of tin is between about 10 and about 30 atomic percent, the concentration of copper is between about 20 and about 40 atomic percent, and the concentration of molybdenum is between about 10 and about 30 atomic percent.

#### Pt-Rh-W-Cu-Mo electrocatalysts

In accordance with one embodiment of the present invention, the catalyst comprises platinum, rhodium, tungsten, copper, and molybdenum. In another embodiment the catalyst is an alloy that consists essentially of the platinum, rhodium, tungsten, copper, and molybdenum.

It has been discovered that improved electrocatalytic activity (e.g., relative activity compared to platinum and/or activity per weight fraction of platinum) is achieved by controlling the relative concentrations of the various metals. In several Pt-Rh-W-Cu-Mo embodiments the concentrations of platinum, rhodium, tungsten, copper, and molybdenum correspond to those concerning the concentrations of platinum, rhodium, and at least one tungsten, tin, copper, and optionally molybdenum set forth herein. Additionally, in one embodiment the concentration of platinum is between about 10 and about 25 atomic percent, the concentration of rhodium is between about 10 and about 25 atomic percent, the concentration of tungsten is between about 10 and about 25 atomic percent, the concentration of copper is between about 25 and about 40 atomic percent, and the concentration of molybdenum is between about 10 and about 25 atomic percent.

#### Formation of an Electrocatalyst Alloy

The electrocatalyst alloys of the present invention may be formed by a variety of methods. For example, the appropriate amounts of the constituents may be mixed together and heated to a temperature above the respective melting points to form a molten solution of the metals which is cooled and allowed to solidify. Typically, electrocatalysts are used in a powder form to increase the surface area which increases the number of reactive sites and leads to improved efficiency of the cell. Thus, the formed metal alloy may be transformed into a powder after being solidified (e.g., by grinding) or during solidification (e.g., spraying molten alloy and

allowing the droplets to solidify). It may, however, be advantageous to evaluate alloys for electrocatalytic activity in a non-powder form (see, Examples 1 and 2, *infra*).

5 To further increase surface area and efficiency, an electrocatalyst alloy for use in a fuel cell may be deposited over the surface of electrically conductive supports (e.g., carbon black). One method for loading an electrocatalyst alloy onto supports typically comprises depositing metal precursor compounds onto the supports, and converting the precursor compounds to metallic form and alloying the metals using a heat-treatment in a reducing atmosphere (e.g., an atmosphere  
10 comprising an inert gas such as argon). One method for depositing the precursor compounds involves chemical precipitation of precursor compounds onto the supports. The chemical precipitation method is typically accomplished by mixing supports and sources of the precursor compounds (e.g., an aqueous solution comprising one or more inorganic metallic salts) at a concentration sufficient to  
15 obtain the desired loading of the electrocatalyst on the supports and then precipitation of the precursor compounds is initiated (e.g., by adding an ammonium hydroxide solution). The slurry is then typically filtered from the liquid under vacuum, washed with deionized water, and dried to yield a powder that comprises the precursor compounds on the supports.

20 Another method for depositing the precursor compounds comprises forming a suspension comprising a solution and supports suspended therein, wherein the solution comprises a solvent portion and a solute portion that comprises the constituents of the precursor compound(s) being deposited. The suspension is frozen to deposit (e.g., precipitate) the precursor compound(s) on the particles. The  
25 frozen suspension is freeze-dried to remove the solvent portion and leave a freeze-dried powder comprising the supports and the deposits of the precursor compound(s) on the supports.

The temperature reached during the thermal treatment is typically at least as high as the decomposition temperature(s) for the precursor compound(s) and not be  
30 so high as to result in degradation of the supports and agglomeration of the supports and/or the electrocatalyst deposits. Typically the temperature is between about 60 °C and about 1100 °C. Inorganic metal-containing compounds typically decompose at temperatures between about 600 and about 1000 °C.

The duration of the heat treatment is typically at least sufficient to  
35 substantially convert the precursor compounds to the desired state. In general, the temperature and time are inversely related (i.e., conversion is accomplished in a shorter period of time at higher temperatures and vice versa). At the temperatures typical for converting the inorganic metal-containing compounds to a metal alloy set forth above, the duration of the heat treatment is typically at least about 30 minutes.  
40 In one embodiment, the duration is between about 2 and about 8 hours.

### Unsupported Catalyst or Alloys in Electrode/Fuel Cell Applications

It is to be noted that, in another embodiment of the present invention, the metal substance (e.g., catalyst or alloy) may be unsupported; that is, it may be employed in the absence of a support particle. More specifically, it is to be noted that in another embodiment of the present invention a metal catalyst or alloy, comprising platinum, rhodium, and tungsten, molybdenum, tin, and/or copper, may be directly deposited (e.g., sputtered) onto, for example, (i) a surface of one or both of the electrodes (e.g., the anode, the cathode or both), and/or (ii) one or both surfaces of a polyelectrolyte membrane, and/or (iii) some other surface, such as a backing for the membrane (e.g., carbon paper).

In this regard it is to be further noted that each component (e.g., metal) of the catalyst or alloy may be deposited separately, each for example as a separate layer on the surface of the electrode, membrane, etc. Alternatively, two or more components may be deposited at the same time. Additionally, in the case of an alloy, the alloy may be formed and then deposited, or the components thereof may be deposited and then the alloy subsequently formed thereon.

Deposition of the component(s) may be achieved using means known in the art, including for example known sputtering technique (see, e.g., PCT Application No. WO 99/16137). Generally speaking, however, in one approach sputter-deposition is achieved by creating, within a vacuum chamber in an inert atmosphere, a voltage differential between a target component material and the surface onto which the target component is to be deposited, in order to dislodge particles from the target component material which are then attached to the surface of, for example, an electrode or electrolyte membrane, thus forming a coating of the target component thereon. In one embodiment, the components are deposited on a polymeric electrolyte membrane, including for example (i) a copolymer membrane of tetrafluoroethylene and perfluoropolyether sulfonic acid (such as the membrane material sold under the trademark NAFION), (ii) a perfluorinated sulfonic acid polymer (such as the membrane material sold under the trademark ACIPLEX), (iii) polyethylene sulfonic acid polymers, (iv) polyketone sulfonic acids, (v) polybenzimidazole doped with phosphoric acid, (vi) sulfonated polyether sulfones, and (vii) other polyhydrocarbon-based sulfonic acid polymers.

It is to be noted that the specific amount of each metal or component of the catalyst or alloy may be controlled independently, in order to tailor the composition to a given application. In some embodiments, however, the amount of each deposited component may be less than about 5 mg/cm<sup>2</sup> of surface area (e.g., electrode surface area, membrane surface area, etc.), less than about 1 mg/cm<sup>2</sup>, less than about 0.5 mg/cm<sup>2</sup>, less than about 0.1 mg/cm<sup>2</sup>, or even less than about 0.05 mg/cm<sup>2</sup>. Alternatively, in some embodiments the amount of the deposited



component, or alloy, may range from about 0.5 mg/cm<sup>2</sup> to less than about 5 mg/cm<sup>2</sup>, or from about 0.1 mg/cm<sup>2</sup> to less than about 1 mg/cm<sup>2</sup>.

It is to be further noted that the specific amount of each component, and/or the conditions under which the component is deposited, may be controlled in order to control the resulting thickness of the component, or alloy, layer on the surface of the electrode, electrolyte membrane, etc. For example, as determined by means known in the art (e.g., scanning electron microscopy or Rutherford back scattering spectrophotometric method), the deposited layer may have a thickness ranging from several angstroms (e.g., about 2, 4, 6, 8, 10 or more) to several tens of angstroms (e.g., about 20, 40, 60, 80, 100 or more), up to several hundred angstroms (e.g., about 200, 300, 400, 500 or more). Additionally, after all of the components have been deposited, and/or alloyed (or, alternatively, after the alloy has been deposited), the layer of the multi-component metal substance of the present invention may have a thickness ranging from several tens of angstroms (e.g., about 20, 40, 60, 80, 100 or more), up to several hundred angstroms (e.g., about 200, 400, 600, 800, 1000, 1500 or more). Thus, in different embodiments the thickness may be, for example, between about 10 and about 500 angstroms, between about 20 and about 200 angstroms, and between about 40 and about 100 angstroms.

It is to be still further noted that in embodiments wherein a catalyst or alloy (or the components thereof) are deposited as a thin film on the surface of, for example, an electrode or electrolyte membrane, the composition of the deposited catalyst or alloy may be as previously described herein.

#### Incorporation of the Electrocatalyst Compositions in a Fuel Cell

Although the alloy compositions of the present invention can be used in any type of fuel cell (e.g., phosphoric acid, molten carbonate, solid oxide, potassium hydroxide, and proton exchange membrane), they are particularly suited for use in proton exchange membrane fuel cells. As shown in FIGS. 1 and 2, a fuel cell, generally indicated **21**, comprises a fuel electrode (anode) **2** and an air electrode, oxidizer electrode (cathode) **3**. In between the electrodes **2** and **3**, a proton exchange membrane **1** serves as an electrolyte and it is usually a strongly acidic ion exchange membrane such as a perfluorosulphonic acid-based membrane. Preferably, the proton exchange membrane **1**, the anode **2**, and the cathode **3** are integrated into one body to minimize contact resistance between the electrodes and the proton exchange membrane. Current collectors **4** and **5** engage the anode and the cathode, respectively. A fuel chamber **8** and an air chamber **9** contain the respective reactants and are sealed by sealants **6** and **7**, respectively.

In general, electricity is generated by hydrogen-containing fuel combustion (i.e., the hydrogen-containing fuel and oxygen react to form water, carbon dioxide and electricity). This is accomplished in the above-described fuel cell by introducing

the hydrogen-containing fuel **F** into the fuel chamber **8**, while oxygen **O** (preferably air) is introduced into the air chamber **9**, whereby an electric current can be immediately transferred between the current collectors **4** and **5** through an outer circuit (not shown). Ideally, the hydrogen-containing fuel is oxidized at the anode **2** to produce hydrogen ions, electrons, and possibly carbon dioxide gas. The hydrogen ions migrate through the strongly acidic proton exchange membrane **1** and react with oxygen and electrons transferred through the outer circuit to the cathode **3** to form water. If the hydrogen-containing fuel **F** is methanol, it is preferably introduced as a dilute acidic solution to enhance the chemical reaction, thereby increasing power output (e.g., a 0.1 M methanol/0.5 M sulfuric acid solution).

To prevent the loss of ionic conduction in the proton exchange membranes, they typically remain hydrated during operation of the fuel cell. As a result, the material of the proton exchange membrane is typically selected to be resistant to dehydration at temperatures up to between about 100 and about 120 °C. Proton exchange membranes usually have reduction and oxidation stability, resistance to acid and hydrolysis, sufficiently low electrical resistivity (e.g.,  $<10 \Omega \cdot \text{cm}$ ), and low hydrogen or oxygen permeation. Additionally, proton exchange membranes are usually hydrophilic. This ensures proton conduction (by reversed diffusion of water to the anode), and prevents the membrane from drying out thereby reducing the electrical conductivity. For the sake of convenience, the layer thickness of the membranes is typically between 50 and 200  $\mu\text{m}$ . In general, the foregoing properties are achieved with materials which have no aliphatic hydrogen-carbon bonds, which, for example, are achieved by replacing hydrogen with fluorine or by the presence of aromatic structures; the proton conduction results from the incorporation of sulfonic acid groups (high acid strength). Suitable proton-conducting membranes also include perfluorinated sulfonated polymers such as NAFION and its derivatives produced by E.I. du Pont de Nemours & Co., Wilmington, Delaware. NAFION is based on a copolymer made from tetrafluoroethylene and perfluorovinylether, and is provided with sulfonic groups working as ion-exchanging groups. Other suitable proton exchange membranes are produced with monomers such as perfluorinated compounds (e.g., octafluorocyclobutane and perfluorobenzene), or even monomers with C—H bonds which, in a plasma polymer, do not form any aliphatic H atoms which could constitute attack sites for oxidative breakdown.

The electrodes of the present invention comprise the electrocatalyst compositions of the present invention and an electrode substrate upon which the electrocatalyst is deposited. In one embodiment the electrocatalyst alloy is directly deposited on the electrode substrate. In another embodiment the electrocatalyst alloy is supported on electrically conductive supports and the supported electrocatalyst is deposited on the electrode substrate. The electrode may also

comprise a proton conductive material that is in contact with the electrocatalyst. The proton conductive material may facilitate contact between the electrolyte and the electrocatalyst, and may thus enhance fuel cell performance. Preferably, the electrode is designed to increase cell efficiency by enhancing contact between the reactant (i.e., fuel or oxygen), the electrolyte and the electrocatalyst. In particular, porous or gas diffusion electrodes are typically used since they allow the fuel/oxidizer to enter the electrode from the face of the electrode exposed to the reactant gas stream (back face), and the electrolyte to penetrate through the face of the electrode exposed to the electrolyte (front face), and reaction products, particularly water, to diffuse out of the electrode.

The electrically conductive support particles typically comprise an inorganic material such as carbon. However, the support particles may comprise an organic material such as an electrically conductive polymer (see, U.S. Pat. Appl. 2002/0132040 A1). Carbon supports may be predominantly amorphous or graphitic and they may be prepared commercially, or specifically treated to increase their graphitic nature (e.g., heat treated at a high temperature in vacuum or in an inert gas atmosphere) thereby increasing corrosion resistance. For example, it may be oil furnace black, acetylene black, graphite paper, carbon fabric, or carbon aerogel. A carbon aerogel preferably has an electrical conductivity of between  $10^{-2}$  and  $10^3 \Omega^{-1} \cdot \text{cm}^{-1}$  and a density of between 0.06 and 0.7 g/cm<sup>3</sup>; the pore size is between 20 and 100 nm (porosity up to about 95%). Carbon black support particles may have a Brunauer, Emmett and Teller (BET) surface area up to about 2000 m<sup>2</sup>/g. It has been reported that satisfactory results are achieved using carbon black support particles having a high mesoporous area, e.g., greater than about 75 m<sup>2</sup>/g (see, Catalysis for Low Temperature Fuel Cells Part 1: The Cathode Challenges, T.R. Ralph and M.P. Hogarth, Platinum Metals Rev., 2002, 46, (1), p. 3-14). Experimental results to date indicate that a surface area of about 500 m<sup>2</sup>/g is preferred.

Preferably, the proton exchange membrane, electrodes, and electrocatalyst materials are in contact with each other. This is typically accomplished by depositing the electrocatalyst either on the electrode, or on the proton exchange membrane, and then placing the electrode and membrane in contact. The alloy electrocatalysts of this invention can be deposited on either the electrode or the membrane by a variety of methods, including plasma deposition, powder application (the powder may also be in the form of a slurry, a paste, or an ink), chemical plating, and sputtering. Plasma deposition generally entails depositing a thin layer (e.g., between 3 and 50  $\mu\text{m}$ , preferably between 5 and 20  $\mu\text{m}$ ) of an electrocatalyst composition on the membrane using low-pressure plasma. By way of example, an organic platinum compound such as trimethylcyclopentadienylplatinum is gaseous between  $10^{-4}$  and 10 mbar and can be excited using radio-frequency, microwaves, or

an electron cyclotron resonance transmitter to deposit platinum on the membrane. According to another procedure, electrocatalyst powder is distributed onto the proton exchange membrane surface and integrated at an elevated temperature under pressure. If, however, the amount of electrocatalyst particles exceeds about 2 mg/cm<sup>2</sup> the inclusion of a binder such as polytetrafluoroethylene is common. Further, the electrocatalyst may be plated onto dispersed small support particles (e.g., the size is typically between 20 and 200 Å, and more preferably between about 20 and 100 Å). This increases the electrocatalyst surface area which in turn increases the number of reaction sites leading to improved cell efficiency. In one such chemical plating process, for example, a powdery carrier material such as conductive carbon black is contacted with an aqueous solution or aqueous suspension (slurry) of compounds of metallic components constituting the alloy to permit adsorption or impregnation of the metallic compounds or their ions on or in the carrier. Then, while the slurry is stirred at high speed, a dilute solution of suitable fixing agent such as ammonia, hydrazine, formic acid, or formalin is slowly added dropwise to disperse and deposit the metallic components on the carrier as insoluble compounds or partly reduced fine metal particles.

The loading, or surface concentration, of an electrocatalyst on the membrane or electrode is based in part on the desired power output and cost for a particular fuel cell. In general, power output increases with increasing concentration; however, there is a level beyond which performance is not improved. Likewise, the cost of a fuel cell increases with increasing concentration. Thus, the surface concentration of electrocatalyst is selected to meet the application requirements. For example, a fuel cell designed to meet the requirements of a demanding application such as an extraterrestrial vehicle will usually have a surface concentration of electrocatalyst sufficient to maximize the fuel cell power output. For less demanding applications, economic considerations dictate that the desired power output be attained with as little electrocatalyst as possible. Typically, the loading of electrocatalyst is between about 0.01 and about 6 mg/cm<sup>2</sup>. Experimental results to date indicate that in some embodiments the electrocatalyst loading is preferably less than about 1 mg/cm<sup>2</sup>, and more preferably between about 0.1 and 1 mg/cm<sup>2</sup>.

To promote contact between the collector, electrode, electrocatalyst, and membrane, the layers are usually compressed at high temperature. The housings of the individual fuel cells are configured in such a way that a good gas supply is ensured, and at the same time the product water can be discharged properly. Typically, several fuel cells are joined to form stacks, so that the total power output is increased to economically feasible levels.

In general, the electrocatalyst compositions and fuel cell electrodes of the present invention may be used to electrocatalyze any fuel containing hydrogen (e.g., hydrogen and reformed-hydrogen fuels). Also, hydrocarbon-based fuels may be

used including saturated hydrocarbons such as methane (natural gas), ethane, propane and butane; garbage off-gas; oxygenated hydrocarbons such as methanol and ethanol; and fossil fuels such as gasoline and kerosene; and mixtures thereof.

To achieve the full ion-conducting property of proton exchange membranes, in some embodiments suitable acids (gases or liquids) are typically added to the fuel. For example, SO<sub>2</sub>, SO<sub>3</sub>, sulfuric acid, trifluoromethanesulfonic acid or the fluoride thereof, also strongly acidic carboxylic acids such as trifluoroacetic acid, and volatile phosphoric acid compounds may be used ("Ber. Bunsenges. Phys. Chem.", Volume 98 (1994), pages 631 to 635).

## Fuel Cell Uses

As set forth above, the alloy compositions of the present invention are useful as electrocatalysts in fuel cells which generate electrical energy to perform useful work. For example, the alloy compositions may be used in fuel cells which are in electrical utility power generation facilities; uninterrupted power supply devices; extraterrestrial vehicles; transportation equipment such as heavy trucks, automobiles, and motorcycles (see, Fuji et al., U.S. Pat. No. 6,048,633; Shinkai et al., U.S. Pat. No. 6,187,468; Fuji et al., U.S. Pat. No. 6,225,011; and Tanaka et al., U.S. Pat. No. 6,294,280); residential power generation systems; mobile communications equipment such as wireless telephones, pagers, and satellite phones (see, Prat et al., U.S. Pat. No. 6,127,058 and Kelley et al., U.S. Pat. No. 6,268,077); mobile electronic devices such as laptop computers, personal data assistants, audio recording and/or playback devices, digital cameras, digital video cameras, and electronic game playing devices; military and aerospace equipment such as global positioning satellite devices; and robots.

## Example 1

### Forming Electrocatalytic Alloys on Individually Addressable Electrodes

The electrocatalyst alloy compositions set forth in Tables A and B, *infra*, were prepared using the combinatorial techniques disclosed in Warren et al., U.S. Pat. No. 6,187,164; Wu et al., U.S. Pat. No. 6,045,671; Strasser, P., Gorer, S. and Devenney, M., *Combinatorial Electrochemical Techniques For The Discovery of New Fuel-Cell Cathode Materials*, Nayayanan, S.R., Gottesfeld, S. and Zawodzinski, T., eds., Direct Methanol Fuel Cells, Proceedings of the Electrochemical Society, New Jersey, 2001, p. 191; and Strasser, P., Gorer, S. and Devenney, M., *Combinatorial Electrochemical Strategies For The Discovery of New Fuel-Cell Electrode Materials*, Proceedings of the International Symposium on Fuel Cells for Vehicles, 41st Battery Symposium, The Electrochemical Society of Japan, Nagoya 2000, p. 153. For example, an array of independent electrodes (with areas of between about 1 and 3 mm<sup>2</sup>) may be fabricated on inert substrates (e.g., glass, quartz, sapphire alumina,

plastics, and thermally treated silicon). The individual electrodes were located substantially in the center of the substrate, and were connected to contact pads around the periphery of the substrate with wires. The electrodes, associated wires, and contact pads were fabricated from a conducting material (e.g., titanium, gold, silver, platinum, copper or other commonly used electrode materials).

Specifically, the alloy compositions set forth in Tables A and B were prepared using a photolithography/RF magnetron sputtering technique (GHz range) to deposit thin-film alloys on arrays of 64 individually addressable electrodes. A quartz insulating substrate was provided and photolithographic techniques were used to design and fabricate the electrode patterns on it. By applying a predetermined amount of photoresist to the substrate, photolyzing preselected regions of the photoresist, removing those regions that have been photolyzed (e.g., by using an appropriate developer), depositing a layer of titanium about 500 nm thick using RF magnetron sputtering over the entire surface and removing predetermined regions of the deposited titanium (e.g. by dissolving the underlying photoresist), intricate patterns of individually addressable electrodes were fabricated on the substrate.

Referring to FIG. 3, the fabricated array 20 consisted of 64 individually addressable electrodes 21 (about 1.7 mm in diameter) arranged in an 8 x 8 square that were insulated from each other (by adequate spacing) and from the substrate 24 (fabricated on an insulating substrate), and whose interconnects 22 and contact pads 23 were insulated from the electrochemical testing solution (by the hardened photoresist or other suitable insulating material).

After the initial array fabrication and prior to depositing the electrocatalyst alloys for screening, a patterned insulating layer covering the wires and an inner portion of the peripheral contact pads, but leaving the electrodes and the outer portion of the peripheral contact pads exposed (preferably approximately half of the contact pad is covered with this insulating layer) was deposited. Because of the insulating layer, it is possible to connect a lead (e.g., a pogo pin or an alligator clip) to the outer portion of a given contact pad and address its associated electrode while the array is immersed in solution, without having to worry about reactions that can occur on the wires or peripheral contact pads. The insulating layer was a hardened photoresist, but any other suitable material known to be insulating in nature could have been used (e.g., glass silica, alumina, magnesium oxide, silicon nitride, boron nitride, yttrium oxide, or titanium dioxide).

Following the creation of the titanium coated array, a steel mask having 64 holes (1.7 mm in diameter) was pressed onto the substrate to prevent deposition of sputtered material onto the insulating resist layer. The deposition of the electrocatalyst alloys was also accomplished using RF magnetron sputtering and a two shutter masking system as described by Wu et al. which enable the deposition of material onto 1 or more electrodes at a time. Each individual thin-film

electrocatalyst alloy is created by a super lattice deposition method. For example, when preparing a ternary alloy electrocatalyst composition, metals M1, M2 and M3 are to be deposited and alloyed onto one electrode. First, a metal M1 sputter target is selected and a thin film of M1 having a defined thickness is deposited on the electrode. This initial thickness is typically from about 3 to about 12 Å. After this, metal M2 is selected as the sputter target and a layer of M2 is deposited onto the layer of M1. The thickness of M2 layer is also from about 3 to about 12 Å. The thicknesses of the deposited layers are in the range of the diffusion length of the metal atoms (e.g., about 10 to about 30 Å) which allows in-situ alloying of the metals. Then, a layer of M3 is deposited onto the M1-M2 alloy forming a M1-M2-M3 alloy film. As a result of the three deposition steps, an alloy thin-film (9 - 25 Å thickness) of the desired stoichiometry is created. This concludes one deposition cycle. In order to achieve the desired total thickness of a cathode electrocatalysts material, deposition cycles are repeated as necessary which results in the creation of a super lattice structure of a defined total thickness (typically about 700 Å). Although the number, thickness (stoichiometry) and order of application of the individual metal layers may be determined manually, it is desirable to utilize a computer program to design an output file which contains the information necessary to control the operation of the sputtering device during the preparation of a particular library wafer (i.e., array). One such computer program is the LIBRARY STUDIO software available from Symyx Technologies, Inc. of Santa Clara, California and described in European Patent No. 1080435 B1. The compositions of several as sputtered alloy compositions were analyzed using x-ray fluorescence (XRF) to confirm that they were consistent with desired compositions (chemical compositions determined using x-ray fluorescence are within about 5% of the actual composition).

Arrays were prepared to evaluate the specific alloy compositions set forth in Tables A and B below. On each array one electrode consisted essentially of platinum and it served as an internal standard for the screening operation.

Table A

Electrode Number	End Current Density (Absolute Activity) mA/cm <sup>2</sup>	End Current Density / Weight Fraction of Pt	Relative Activity Compared to Internal Pt	Pt atomic %	Rh atomic %	W atomic %	Mo atomic %	Sn atomic %	Cu atomic %
20	-2.119	-9.244	4.832	20	20	60	0	0	0
12	-1.563	-5.399	3.565	20	20	20	40	0	0
15	-1.245	-3.528	2.840	20	20	0	40	0	20
56	-1.242	-5.052	2.833	17	17	33	0	0	33
28	-1.030	-3.789	2.349	20	20	20	0	40	0
10	-0.964	-3.001	2.199	20	20	0	40	20	0
18	-0.927	-3.727	2.114	20	20	40	0	20	0
23	-0.802	-3.003	1.830	20	20	40	0	0	20
53	-0.601	-2.171	1.371	17	17	17	17	0	33
49	-0.446	-1.459	1.018	17	17	0	17	17	33
3	-0.438	-0.438	1.000	100	0	0	0	0	0
7	-0.428	-0.550	0.977	60	20	0	0	0	20
4	-0.421	-0.627	0.960	60	20	20	0	0	0
45	-0.414	-0.821	0.945	40	20	20	20	0	0
51	-0.404	-0.642	0.922	40	20	0	0	0	40
63	-0.395	-0.660	0.901	40	20	0	20	0	20
48	-0.394	-0.871	0.899	40	20	40	0	0	0
60	-0.378	-0.750	0.863	40	20	20	20	0	0
44	-0.369	-0.738	0.842	40	40	20	0	0	0
47	-0.353	-0.597	0.806	40	40	0	0	0	20
41	-0.335	-0.606	0.763	40	20	0	20	20	0
36	-0.332	-1.170	0.757	20	60	20	0	0	0
58	-0.325	-0.587	0.740	40	20	0	20	20	0

5

10

15

20

25



52	-0.312	-1.140	0.713	17	33	17	0	0	33
55	-0.303	-0.917	0.691	17	33	0	0	0	50
40	-0.298	-1.174	0.679	20	40	40	0	0	0
39	-0.267	-0.777	0.610	20	60	0	0	0	20
2	-0.261	-0.360	0.596	60	20	0	20	0	0
42	-0.248	-0.453	0.565	40	40	0	0	20	0
34	-0.217	-0.691	0.495	20	60	0	0	20	0
46	-0.216	-0.403	0.492	40	20	0	0	40	0
37	-0.216	-0.752	0.492	20	40	20	20	0	0
50	-0.206	-0.681	0.470	17	33	0	0	17	33
33	-0.144	-0.454	0.329	20	40	0	20	20	0
38	-0.124	-0.404	0.283	20	40	0	0	40	0
31	-0.108	-0.329	0.245	20	20	0	0	40	20
54	-0.102	-0.345	0.233	17	17	0	0	33	33
26	-0.085	-0.283	0.193	20	20	0	0	60	0

5

10

15

Table B

## Pt—Rh—W Alloy Compositions

	Electrode Number	End Current Density (Absolute Activity)	End Current Density / Weight Fraction of Pt	Relative Activity Compared to Internal Pt	Pt	Rh	W
		mA/cm <sup>2</sup>			atomic %	atomic %	atomic %
5	23	-2.630	-7.467	9.700	32.03	12.37	55.60
	22	-2.213	-9.240	8.164	20.42	24.50	55.08
	6	-2.133	-16.793	7.866	10.92	21.48	67.60
	13	-1.626	-12.293	5.998	10.80	31.87	57.33
10	5	-1.469	-8.259	5.420	14.89	27.47	57.64
	21	-1.375	-21.057	5.071	5.14	37.96	56.89
	14	-0.913	-14.706	3.369	5.21	25.63	69.16
	15	-0.553	-2.415	2.040	20.67	12.40	66.92
	7	-0.468	-7.898	1.725	5.28	12.98	81.74
15	20	-0.467	-3.384	1.723	10.68	42.05	47.27
	4	-0.444	-2.039	1.636	17.84	31.92	50.23
	12	-0.364	-1.973	1.341	14.75	36.29	48.95
	29	-0.339	-1.349	1.250	20.17	36.30	43.53
	64	-0.271	-0.271	1.000	100.00	0.00	0.00
20	31	-0.255	-0.540	0.942	43.32	12.33	44.35
	3	-0.244	-0.979	0.900	20.13	35.36	44.52
	30	-0.240	-0.653	0.887	31.64	24.43	43.93
	11	-0.227	-1.010	0.837	17.70	39.58	42.71
	46	-0.224	-0.363	0.828	53.88	24.28	21.84
25	1	-0.217	-0.731	0.801	23.42	40.32	36.26
	10	-0.217	-0.846	0.800	19.98	42.13	37.89
	2	-0.217	-0.787	0.799	21.94	38.09	39.97
	39	-0.214	-0.361	0.788	54.55	12.29	33.16
	19	-0.209	-1.091	0.770	14.62	44.95	40.43
30	47	-0.207	-0.292	0.762	65.70	12.26	22.04
	36	-0.202	-0.765	0.744	19.93	47.82	32.25
	37	-0.201	-0.522	0.743	31.25	36.20	32.55
	9	-0.200	-0.709	0.739	21.80	44.16	34.04
	38	-0.198	-0.401	0.730	42.79	24.36	32.85
35	28	-0.196	-2.844	0.722	5.08	49.98	44.94
	27	-0.195	-1.354	0.720	10.57	52.01	37.42
	18	-0.189	-0.813	0.696	17.56	47.12	35.31
	45	-0.185	-0.358	0.682	42.27	36.09	21.64
	26	-0.181	-0.913	0.669	14.49	53.46	32.05
40	34	-0.168	-1.112	0.620	10.46	61.77	27.77
	44	-0.165	-0.407	0.608	30.88	47.68	21.44
	25	-0.159	-0.664	0.587	17.42	54.55	28.03
	43	-0.142	-0.511	0.524	19.69	59.06	21.25
	33	-0.141	-0.681	0.520	14.36	61.82	23.82
45	41	-0.131	-0.827	0.484	10.36	71.32	18.32
	35	-0.131	-1.803	0.484	5.02	61.70	33.29
	42	-0.123	-1.597	0.455	4.95	73.13	21.92

17	-0.084	-0.318	0.310	19.84	48.84	31.35
----	--------	--------	-------	-------	-------	-------

### Example 2

#### Screening Alloys for Electrocatalytic Activity

The alloy compositions set forth in Tables A and B (set forth above) that were synthesized on arrays according to the method set forth in Example 1 were screened for the electrochemical reduction of molecular oxygen to water to determine relative electrocatalytic activity against the internal and/or external platinum standard.

In general, the array wafers were assembled into an electrochemical screening cell and a screening device established an electrical contact between the 64 electrode electrocatalysts (working electrodes) and a 64-channel multi channel potentiostat used for the screening. Specifically, each wafer array was placed into a screening device such that all 64 spots are facing upward and a tube cell body that was generally annular and having an inner diameter of about 2 inches (5 cm) was pressed onto the upward facing wafer surface. The diameter of this tubular cell was such that the portion of the wafer with the square electrode array formed the base of a cylindrical volume while the contact pads were outside the cylindrical volume. A liquid ionic solution (electrolyte) was poured into this cylindrical volume and a common counter electrode (i.e., platinum gauze), as well as a common reference electrode (e.g., mercury/mercury sulfate reference electrode (MMS)), were placed into the electrolyte solution to close the electrical circuit.

A rotator shaft with blades was also placed into the electrolyte to provide forced convection-diffusion conditions during the screening. The rotation rate was typically between about 300 to about 400 rpm. Depending on the screening experiment either argon or pure oxygen was bubbled through the electrolyte during the measurements. Argon served to remove  $O_2$  gas in the electrolyte to simulate  $O_2$ -free conditions used for the initial conditioning of the electrocatalysts. The introduction of pure oxygen served to saturate the electrolyte with oxygen for the oxygen reduction reaction. During the screening, the electrolyte was maintained at 60 °C and the rotation rate was constant. Three groups of tests were performed to screen the activity of the electrocatalysts. The electrolyte (1 M  $HClO_4$ ) was purged with argon for about 20 minutes prior to the electrochemical measurements. The first group of tests comprised cyclic voltammetric measurements while purging the electrolyte with argon. Specifically, the first group of tests comprised:

- a. a potential sweep from about OCP to about ~~+0.3 V~~ to about ~~-0.63 V~~ and back to about +0.3 V at a rate of about 20 mV/s;
- b. twelve consecutive potential sweeps from OCP to about +0.3 V to about -0.7 V and back to about +0.3 V at a rate of about 200 mV/s; and
- c. a potential sweep from about OCP to about +0.3 V to about -0.63 V and back to about +0.3 V at a rate of about 20 mV/s.

5 The electrolyte was then purged with oxygen for approximately 30 minutes. The following second group of tests were performed while continuing to purge with  
10 oxygen:

- a. measuring the open circuit potential (OCP) for a minute; then, starting at OCP the voltage was swept down to about -0.4 V at a rate of about 10 mV/s;
- b. measuring the OCP for a minute; then applying a potential step from  
15 OCP to about +0.1 V while measuring the current for about 5 minutes; and
- c. measuring the OCP for a minute; then applying a potential step from OCP to about +0.2 V while monitoring the current for about 5 minutes.

The third group of tests comprised a repeat of the second group of tests after about  
20 one hour from completion of the second group of tests. The electrolyte was continually stirred and purged with oxygen during the waiting period. All the foregoing test voltages are with reference to a mercury/mercury sulfate (MMS) electrode. Additionally, an external platinum standard comprising an array of 64 platinum electrodes in which the oxygen reduction activity of the 64 platinum  
25 electrodes averaged -0.35 mA/cm<sup>2</sup> at +0.1V vs. a mercury/mercury sulfate electrode was used to monitor the tests to ensure the accuracy of the oxygen reduction evaluation.

The specific alloy compositions set forth in Tables A and B were prepared and screened in accordance with the above-described methods and the results are  
30 set forth therein. The screening results in Tables A and B are for the third test group steady state currents at +0.1 V MMS. The current value reported (End Current Density) is the result of averaging the last three current values of the chronoamperometric test normalized for geometric surface area. Referring to Table A, the alloys corresponding to Electrode Numbers 20, 12, 15, 56, 28, 10, 18, 23, 53,  
35 and 49 exhibited an oxygen reduction activity greater than the internal platinum

standard. Additionally, although having an oxidation activity that was less than the internal platinum standard, the alloys corresponding to Electrode Numbers 7, 4, 45, 51, 63, 48, 60, 44, 47, 41, 36, 58, 52, 55, 40, 39, 42, 34, 37, 50, and 33 had an end current density (or activity) per weight fraction of platinum that exceeded the platinum standard (100% platinum). Referring to Table B, the Pt-Rh-W alloy compositions corresponding to Electrode Numbers 23, 22, 6, 13, 5, 21, 14, 15, 7, 20, 4, 12, and 29 exhibited an oxygen reduction activity greater than the internal platinum standard. Further, all the alloys set forth in Table B had an end current density (or activity) per weight fraction of platinum that exceeded the platinum standard (100% platinum).

### Example 3

#### Synthesis of Supported Electrocatalyst Alloys

The synthesis of  $\text{Pt}_{32}\text{Rh}_{12}\text{W}_{56}$  and  $\text{Pt}_{20}\text{Rh}_{20}\text{Mo}_{40}\text{Sn}_{20}$  (see, Table C, Target Catalyst Comp., *infra*) on carbon support particles was attempted according to different process conditions in order to evaluate the performance of the alloys while in a state that is typically used in fuel cell. To do so, the alloy component precursors were deposited or precipitated on supported platinum powder (i.e., platinum nanoparticles supported on carbon black particles). Platinum supported on carbon black is commercially available from companies such as Johnson Matthey, Inc., of New Jersey and E-Tek Div. of De-Nora, N.A., Inc., of Somerset, New Jersey. Such supported platinum powder is available with a wide range of platinum loading. The supported platinum powder used in this example had a nominal platinum loading of about 40 percent by weight, a platinum surface area of between about 150 and about 170  $\text{m}^2/\text{g}$  (determined by CO adsorption), a combined carbon and platinum surface area between about 350 and about 400  $\text{m}^2/\text{g}$  (determined by  $\text{N}_2$  adsorption), and an average particle size of less than about 0.5  $\mu\text{m}$  (determined by sizing screen).

Referring to Table C, the electrocatalyst alloys corresponding to the target compositions of  $\text{Pt}_{32}\text{Rh}_{12}\text{W}_{56}$  (HFC 38 and 39) were formed on carbon support particles using a chemical precipitation method according to the following steps. To prepare the HFC 38 and 39 compositions, about 0.25 g of carbon supported platinum powder (37.8 wt% Pt) was dispersed in about 100 mL of room temperature 18 M $\Omega$  deionized water using an ultrasonic blending device (e.g., an AQUASONIC 50 D set at power level 9) for about 2 hours to form a slurry. The slurry was stirred

using a magnetic stirring device, and while being stirred, appropriate volumes based on the targeted electrocatalyst composition of one or more appropriate solutions and/or suspension comprising the metals to be alloyed with the platinum nanoparticles were added drop-wise to the slurry (i.e., a 0.85 ml of 1M tungstic acid colloidal suspension and 0.19 ml of 1M  $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$  solution). The tungstic acid colloidal suspension was prepared by dissolving the tungstic acid in water to form a yellow solution and then adding ammonium hydroxide until the yellow color disappears and the solution became a colloidal suspension. The stirring was continued and the slurries (HFC 38 and 39) were heated to a temperature between about 60 and about 90 °C for about 1 hour. Precipitation of compounds comprising the metals was then initiated by slowly adding a 10 wt % ammonium hydroxide aqueous solution to the slurries until the slurry had a pH of about 10. The slurries were stirred for about 15 more minutes. The slurries were then filtered from the liquid under vacuum after which the filtrate was washed with about 150 mL of deionized water. The powders were then dried at a temperature between about 60 and about 100 °C for about 4 hours to about 8 hours.

Referring to Table C, the electrocatalyst alloys corresponding to HFC 154, 155, 158, 159, 183, and 184 were formed on carbon support particles using a freeze-drying precipitation method. The freeze-drying method comprised forming a precursor solution comprising the desired metal atoms in the desired concentrations. For example, to prepare the target  $\text{Pt}_{20}\text{Rh}_{20}\text{Mo}_{40}\text{Sn}_{20}$  alloy compositions (HFC 154 and 155), about 0.069 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  was dissolved in about 5 ml  $\text{H}_2\text{O}$  and then about 0.144 ml of a  $\text{Rh}(\text{NO}_3)_3$  solution [about 10 wt% Rh solution in  $\text{HNO}_3$ ] was dissolved in the solution. Next, about 0.077 g of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  was added to the solution to yield a white suspension. Then, about 0.2 ml of concentrated  $\text{HNO}_3$  was added to dissolve the suspended portion and produced a clear yellow solution. To prepare the target  $\text{Pt}_{32}\text{Rh}_{12}\text{W}_{56}$  alloy compositions (HFC 183 and 184), about 0.090g of  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$  was added in about 5 ml  $\text{H}_2\text{O}$ . Next, about 0.054 ml of a  $\text{Rh}(\text{NO}_3)_3$  solution [about 10 wt% Rh solution in  $\text{HNO}_3$ ] was added. The suspension was heated at about 100 °C for 2 minutes, which resulted in a clear yellow solution. The HFC 154, 155, 183, and 184 solutions were introduced into separate HDPE (High Density Poly Ethylene) vials containing about 0.200 g of supported platinum powder which had a nominal platinum loading of about 19.2 percent by weight resulting in a black suspension. The suspensions were homogenized by immersing

a probe of a BRANSON SONIFIER 150 into the vial and sonicating the mixture for about 1 minute at a power level of 3.

An alternative synthesis of the target  $\text{Pt}_{20}\text{Rh}_{20}\text{Mo}_{40}\text{Sn}_{20}$  alloy was performed (HFC 158 and 159) by dissolving about 0.069 g of  $(\text{NH}_4)\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  in about 2.5 ml  $\text{H}_2\text{O}$  and then dissolving about 0.144 ml of a  $\text{Rh}(\text{NO}_3)_3$  solution [about 10 wt% Rh solution in  $\text{HNO}_3$ ] to form a first source solution. Next, about 0.077 g of  $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$  was dissolved in about 2.5 ml of  $\text{H}_2\text{O}$  to form a second source solution. The first source solution (the molybdenum and rhodium-containing solution) was introduced into the HDPE vial containing the 0.200 g of supported platinum powder with the same platinum loading, resulting in a black suspension. The suspension was homogenized by immersing a probe of a BRANSON SONIFIER 150 into the vial and sonicating the mixture for about 30 seconds at a power level of 3. Subsequently, the second source solution (the tin-containing solution) was introduced into the vials, which contained the suspensions of the carbon supported platinum, molybdenum and rhodium-containing solution. The suspension was further homogenized by sonicating the mixture for an additional 1 minute at a power level of 3.

The vials containing the homogenized suspensions were then immersed in a liquid nitrogen bath for about 3 minutes to solidify the suspensions. The solid suspensions were then freeze-dried for about 24 hours using a LABONCO FREEZE DRY SYSTEM (Model 79480) to remove the solvent. The tray and the collection coil of the freeze dryer were maintained at about  $26^\circ\text{C}$  and about  $-48^\circ\text{C}$ , respectively, while evacuating the system (the pressure was maintained at about 0.15 mbar). After freeze-drying, each vial contained a powder comprising the supported platinum powder, and rhodium, and tungsten, molybdenum, tin, and/or copper.

The recovered precursor powders (chemically precipitated and freeze-dried) were then subjected to a heat treatment to reduce the precursors to their metallic state, and to alloy the metals with each other and the platinum on the carbon black particles. One particular heat treatment comprised heating the powder in a quartz flow furnace with an atmosphere comprising about 6%  $\text{H}_2$  and 94% Ar using a temperature profile of room temperature to about  $40^\circ\text{C}$  at a rate of about  $5^\circ\text{C}/\text{min}$ ; holding at about  $40^\circ\text{C}$  for 2 hours; increasing the temperature to about  $200^\circ\text{C}$  at a rate of  $5^\circ\text{C}/\text{min}$ ; holding at about  $200^\circ\text{C}$  for two hours; increasing the temperature at a rate of about  $5^\circ\text{C}/\text{min}$  to about  $700$  or  $900^\circ\text{C}$ ; holding at a max temperature of about  $700$  or  $900^\circ\text{C}$  for a duration of about two, three, seven or eight hours (indicated in Table C); and cooling down to room temperature.

In order to determine the actual composition of the supported electrocatalyst alloys, the differently prepared alloys (e.g., by composition variation or by heat treatment variation) were subjected to ICP elemental analysis or subjected to EDS (Electron Dispersive Spectroscopy) elemental analysis. For the latter technique, the sample powders were compressed into 6 mm diameter pellets with a thickness of about 1 mm. The target alloy composition and actual composition for the prepared supported electrocatalyst alloys are also set forth in Table C.



Table C

Powder Name	Target Catalyst Comp.	Max Alloying Temp for a duration (°C / hrs)	Actual Catalyst Comp.	Target Pt Loading (wt%)	Measured Pt Loading (wt%)	Log Pt Mass Activity at +0.15 V MMS	Pt Mass Activity at +0.15 V MMS (mA/mg Pt)	Relative performance at +0.15 V MMS	Catalyst Mass Activity at 0.15 V MMS (mA/mg)
HFC 10	Pt	---	Pt by ICP	37.9	37.9	2.11	128.82	1.00	48.82
HFC 38	Pt <sub>32</sub> Rh <sub>12</sub> W <sub>56</sub>	700 / 3	Pt <sub>50</sub> Rh <sub>45</sub> W <sub>5</sub> by ICP	22	29	1.84	69.19	0.54	20.06
HFC 39	Pt <sub>32</sub> Rh <sub>12</sub> W <sub>56</sub>	700 / 8	Pt <sub>50</sub> Rh <sub>45</sub> W <sub>5</sub> by ICP	22	29	1.95	89.13	0.69	25.85
HFC 154	Pt <sub>20</sub> Rh <sub>20</sub> Mo <sub>40</sub> Sn <sub>20</sub>	700 / 7	Pt <sub>19</sub> Rh <sub>14</sub> Mo <sub>42</sub> Sn <sub>25</sub> by EDS	13.6	12.5	2.30	197.32	1.53	24.66
HFC 155	Pt <sub>20</sub> Rh <sub>20</sub> Mo <sub>40</sub> Sn <sub>20</sub>	900 / 2	---	13.6	---	---	---	---	18.93
HFC 158	Pt <sub>20</sub> Rh <sub>20</sub> Mo <sub>40</sub> Sn <sub>20</sub>	700 / 7	---	13.6	---	---	---	---	18.65
HFC 159	Pt <sub>20</sub> Rh <sub>20</sub> Mo <sub>40</sub> Sn <sub>20</sub>	900 / 2	Pt <sub>18</sub> Rh <sub>19</sub> Mo <sub>40</sub> Sn <sub>23</sub> by EDS	13.6	11.9	2.36	231.39	1.80	27.54
HFC 183	Pt <sub>32</sub> Rh <sub>12</sub> W <sub>56</sub>	700 / 7	Pt <sub>34</sub> Rh <sub>13</sub> W <sub>53</sub> by EDS	14	17.0	2.24	174.83	1.36	29.72
HFC 184	Pt <sub>32</sub> Rh <sub>12</sub> W <sub>56</sub>	900 / 2	---	14	---	---	---	---	16.80

Example 4Evaluating the Electrocatalytic Activity of Supported Electrocatalysts

The supported alloy electrocatalysts set forth in Table C and formed according to Example 3 were subjected to electrochemical measurements to evaluate their activities. For the evaluation, the supported alloy electrocatalysts were applied to a rotating disk electrode (RDE) as is commonly used in the art (see, Rotating disk electrode measurements on the CO tolerance of a high-surface area Pt/Vulcan carbon fuel cell electrocatalyst, Schmidt et al., Journal of the Electrochemical Society (1999), 146(4), 1296-1304; and Characterization of high-surface-area electrocatalysts using a rotating disk electrode configuration, Schmidt et al., Journal of the Electrochemical Society (1998), 145(7), 2354-2358). Rotating disk electrodes are a relatively fast and simple screening tool for evaluating supported electrocatalysts with respect to their intrinsic electrolytic activity for oxygen reduction (e.g., the cathodic reaction of a fuel cell).

The rotating disk electrode was prepared by depositing an aqueous-based ink that comprises the support electrocatalyst and a NAFION solution on a glassy carbon disk. The concentration of electrocatalyst powder in the NAFION solution was about 1 mg/mL. The NAFION solution comprised the perfluorinated ion-exchange resin, lower aliphatic alcohols and water, wherein the concentration of resin is about 5 percent by weight. The NAFION solution is commercially available from the ALDRICH catalog as product number 27,470-4. The glassy carbon electrodes were 5 mm in diameter and were polished to a mirror finish. Glassy carbon electrodes are commercially available, for example, from Pine Instrument Company of Grove City, Pennsylvania. An aliquot of 10  $\mu$ L electrocatalyst suspension was added to the carbon substrate and allowed to dry at a temperature between about 60 and 70 °C. The resulting layer of NAFION and electrocatalyst was less than about 0.2  $\mu$ m thick. This method produced slightly different platinum loadings for each electrode made with a particular suspension, but the variation was determined to be less than about 10 percent by weight.

After being dried, the rotating disk electrode was immersed into an electrochemical cell comprising an aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution maintained at room temperature. Before performing any measurements, the electrochemical cell was purged of oxygen by bubbling argon through the electrolyte for about 20 minutes. All measurements were taken while rotating the electrode at about 2000 rpm, and the measured current densities were normalized either to the

glassy carbon substrate area or to the platinum loading on the electrode. Two groups of tests were performed to screen the activity of the supported electrocatalysts. The first group of tests comprised cyclic voltammetric measurements while purging the electrolyte with argon. Specifically, the first group comprised:

- a. two consecutive potential sweeps starting from OCP to about +0.35V then to about -0.65V and back to OCP at a rate of about 50 mV/s;
- b. two hundred consecutive potential sweeps starting from OCP to about +0.35V then to about -0.65V and back to OCP at a rate of about 200 mV/s; and
- c. two consecutive potential sweeps starting from OCP to about +0.35V then to about -0.65V and back to OCP at a rate of about 50 mV/s.

The second test comprised purging with oxygen for about 15 minutes followed by a potential sweep test for oxygen reduction while continuing to purge the electrolyte with oxygen. Specifically, potential sweeps from about -0.45 V to +0.35 V were performed at a rate of about 5 mV/s to evaluate the initial activity of the electrocatalyst as a function of potential and to create a geometric current density plot. The electrocatalysts were evaluated by comparing the diffusion corrected activity at 0.15 V. All the foregoing test voltages are with reference to a mercury/mercury sulfate electrode. Also, it is to be noted that the oxygen reduction measurements for a glassy carbon RDE without an electrocatalyst did not show any appreciable activity within the potential window.

The above-described supported electrocatalyst alloy compositions were evaluated in accordance with the above-described method and the results are set forth in Table C. The alloy compositions  $\text{Pt}_{19}\text{Rh}_{14}\text{Mo}_{42}\text{Sn}_{25}$  and  $\text{Pt}_{18}\text{Rh}_{19}\text{Mo}_{40}\text{Sn}_{23}$  exhibited oxygen reduction activities greater than that of carbon supported platinum. The results of the evaluation also indicate, among other things, that it may take numerous iterations to develop a set of parameters for producing the target alloy composition. Also evidenced by the data, is that activity can be adjusted by changes in the processing conditions and fuel cell operation conditions.

Further, without being held to a particular theory, it is presently believed that differences in activity for similar alloy compositions may be due to several factors such as alloy homogeneity (e.g., an alloy, as defined below, may have regions in which the constituent atoms show a presence or lack of order, i.e., regions of solid solution within an ordered lattice, or some such superstructure), changes in the

lattice parameter due to changes in the average size of component atoms, changes in particle size, and changes in crystallographic structure/symmetry. The ramifications of structure and symmetry changes are often difficult to predict. Platinum and rhodium have a face-centered cubic (fcc) structure. In contrast, tungsten and molybdenum typically crystallize in a body-centered cubic (bcc) structure, however, other structures are also possible. The various structures of tin are often more complex. Pt-Rh alloys may form complete solid solutions based on the similarities of the end members. Pt-W alloys may form solid solutions, however, at least one unique Pt-W alloy is also known to exist. Pt-Mo alloys are known in a variety of compositions and symmetries, while the Pt-Sn system displays still more structure types. When ternary systems are considered, the phase space becomes increasingly complex. Clearly, symmetry variations are to be expected across a multi-component compositional range within these systems. An example from a less complex system, Pt-Fe, displays the types of variations that may be expected. For example, in the Pt-Fe system, as the amount of iron added to platinum increases, the lattice of the resulting alloy may be expected to change from an fcc lattice to a tetragonal primitive lattice. More specifically, the possibility exists that as the relative ratio of metal (in this case Fe) to platinum goes from 0 to 1, an fcc-based solid solution first occurs (e.g., Fe and Pt may mix randomly within some concentration limits, or under some specific synthesis conditions), and out of this solid solution an ordered phase may gradually crystallize (e.g.,  $\text{Pt}_3\text{Fe}$ , primitive cubic structure) only to return to a solid solution (disordered alloy) and again back to an ordered phase (now with either a primitive or face-centered tetragonal structure) as the formula  $\text{PtFe}$  is achieved. Symmetry changes (e.g., those associated with the changes from a cubic face-centered structure to a primitive tetragonal structure) may result in significant changes in the x-ray diffraction pattern.

In addition to the foregoing crystal structure changes, other subtle changes in lattice parameters may also be indicative of the resulting changes in the size of the respective metal constituents. The 12-coordinate metallic radii of platinum, rhodium, tungsten, molybdenum, copper and tin are 1.39 Å, 1.34 Å, 1.41 Å, 1.40 Å, 1.28 Å and 1.58 Å, respectively, and as metals are substituted for platinum, the average metal radius, and consequently the observed lattice parameter of a disordered alloy may be expected to contract or expand accordingly. Thus, in the case of disordered alloys, the average radius may be used as an indicator of lattice changes as a function of stoichiometry, or alternatively, as an indicator of stoichiometry based on

observed diffraction patterns. However, while the average radii may be useful as a general rule, experimental results are typically expected to conform only in a general manner because local ordering, significant size disparity between atoms, significant changes in symmetry, and other factors may produce results that are inconsistent with expectations. This may be particularly true in the case of ordered alloys where an increase in the directionality of bonding may occur.

Interpretations of XRD analyses for the foregoing supported alloys are set forth below. An interpretation of an XRD analysis tends to be subjective, and therefore, the following conclusions are not intended to be limiting. The predicted change in the average radius for the  $\text{Pt}_{50}\text{Rh}_{45}\text{W}_5$  alloys (HFC 38 and 39) was a contraction of 1.3% versus platinum. The XRD pattern, however, showed a mixed phase material that may include partially substituted Pt. The material alloy comprises particles that were ~5.6 nm in size.

The predicted change in the average radius for the  $\text{Pt}_{19}\text{Rh}_{14}\text{Mo}_{42}\text{Sn}_{25}$  alloys (HFC 154 and 155) was an expansion of 3.4% vs. platinum. The XRD pattern, however, showed a mixed phase material that may include partially substituted Pt. Although prepared in a slightly different manner, HFC 158 and 159 are compositionally similar to HFC 154 and 155 ( $\text{Pt}_{18}\text{Rh}_{19}\text{Mo}_{40}\text{Sn}_{23}$ ). These materials display very similar XRD patterns, the primary difference being in the degree of crystallinity. The electrochemical performance set forth in Table C is also similar.

The predicted change in the average radius for the  $\text{Pt}_{34}\text{Rh}_{13}\text{W}_{53}$  alloys (HFC 183 and 184) was an expansion of 0.6% vs. platinum. The XRD determined expansion of HFC 183 and 184 was about 0.5%. HFC 183 and 184 display the structural characteristics of a disordered alloy. The calculated particle sizes for HFC 183 and 184 were approximately 2.6 nm.

In view of the foregoing, for a particular electrocatalyst composition a determination of the optimum conditions is preferred to produce the highest activity for that particular composition. For example, the starting materials used to synthesize the alloy may play a role in the activity of the synthesized alloy. Specifically, using something other than a metal nitrate salt solution to supply the metal atoms may result in different activities. Different methods of synthesis (e.g., chemical precipitation and freeze-drying impregnation) may result in differing activities due to both differences in particle size and/or differences in stoichiometric control. Heat treatment parameters such as atmosphere, time, temperature, etc. may also need to be optimized. This optimization may involve balancing competing

phenomena. For example, increasing the heat treatment temperature is generally known to improve the reduction of a metal salt to a metal which typically increases activity; however, it also tends to increase the size of the electrocatalyst alloy particle and decrease surface area, which decreases electrocatalytic activity.

5

### Definitions

Activity is defined as the maximum sustainable, or steady state, current (Amps) obtained from the electrocatalyst, when fabricated into an electrode, at a given electric potential (Volts). Additionally, because of differences in the geometric area of electrodes, when comparing different electrocatalysts, activity is often  
10 expressed in terms of current density ( $A/cm^2$ ).

An alloy is a mixture comprising two or more metals. An alloy may be described as a solid solution in which the solute and solvent atoms (the term solvent is applied to the metal that is in excess) are arranged at random, much in the same way as a liquid solution may be described. If some solute atoms replace some of  
15 those of the solvent in the structure of the latter, the solid solution may be defined as a substitutional solid solution. Alternatively, an interstitial solid solution is formed if a smaller atom occupies the interstices between the larger atoms. Combinations of the two types are also possible. Furthermore, in certain solid solutions, some level of regular arrangement may occur under the appropriate conditions resulting in a  
20 partial ordering that may be described as a superstructure. These solid solutions may have characteristics that may be distinguishable through characterization techniques such as XRD. Significant changes in XRD may be apparent due to changes in symmetry, if more complete ordering occurs such as that which occurs between Pt metal and  $Pt_3Fe$ . Although the global arrangement of the atoms is  
25 extremely similar in both cases, the relationship between the locations of the Pt and Fe atoms is now ordered and not random resulting in different diffraction patterns. Further, a homogeneous alloy is a single compound comprising the constituent metals. A heterogeneous alloy comprises an intimate mixture of crystals of individual metals and/or metallic compounds (see, Structural Inorganic Chemistry,  
30 A.F. Wells, Oxford University Press, 5<sup>th</sup> Edition, 1995, chapter 29). An alloy, as defined herein, is also meant to include materials which may comprise elements which are generally considered to be non-metallic. For example, some alloys of the present invention may comprise oxygen in atomic, molecular, and/or metallic oxide form. Additionally, some alloys of the present invention may comprise carbon in

atomic, molecular, and/or metal carbide form. If present, the amount of oxygen and/or carbon in the alloy is typically at what is generally considered to be a low or impurity level (e.g., less than about 5, 1, 0.5, or 0.1 atomic percent).

- 5 It is to be understood that the above description is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should therefore be determined not with reference to the above description alone, but should be determined with reference to the claims and the full scope of equivalents to which such claims are entitled.

WHAT IS CLAIMED IS

1. A catalyst for use in oxidation or reduction reactions, the catalyst comprising platinum, rhodium, at least one of tungsten, tin, and copper, and optionally molybdenum, in metallic oxidation states, provided the platinum and rhodium are at concentrations such that the sum of said concentrations is no greater  
5 than 85 atomic percent.
2. The catalyst of claim 1 consisting essentially of platinum, rhodium, at least one of tungsten, tin, and copper, and optionally molybdenum.
3. The catalyst of claim 1 wherein the concentration of platinum is between about 5 and 85 atomic percent.
4. The catalyst of claim 1 wherein the concentration of rhodium is between about 5 and 85 atomic percent.
5. The catalyst of claim 1 wherein tungsten, tin, copper, molybdenum, or a combination thereof is at a concentration that is between 15 and about 90 atomic percent.
6. The catalyst of claim 1 wherein the concentration of platinum is between about 10 and about 75 atomic percent, the concentration of rhodium is between about 10 and about 75 atomic percent, and tungsten, tin, copper, molybdenum, or a combination thereof is at a concentration that is between about 20 and about 80  
5 atomic percent.
7. The catalyst of claim 1 wherein the concentration of platinum is between about 5 and about 50 atomic percent, the concentration of rhodium is between about 5 and about 50 atomic percent, and tungsten is at a concentration that is between about 40 and about 85 atomic percent.
8. The catalyst of claim 1 wherein the concentration of platinum is between about 10 and about 45 atomic percent, the concentration of rhodium is between



about 10 and about 40 atomic percent, and tungsten is at a concentration that is between about 45 and about 80 atomic percent.

9. The catalyst of claim 1 wherein the concentration of platinum is between about 15 and about 40 atomic percent, the concentration of rhodium is between about 10 and about 30 atomic percent, and tungsten is at a concentration that is between about 50 and about 70 atomic percent.

10. The catalyst of claim 1 wherein the concentration of platinum is between about 10 and about 40 atomic percent, the concentration of rhodium is between about 5 and about 30 atomic percent, and tungsten is at a concentration that is between about 50 and about 70 atomic percent.

11. The catalyst of claim 1 wherein the concentration of platinum is between about 30 and about 40 atomic percent, the concentration of rhodium is between about 10 and about 20 atomic percent, and tungsten is at a concentration that is between about 50 and about 60 atomic percent.

12. The catalyst of claim 1 wherein the concentration of platinum is between about 10 and about 70 atomic percent, the concentration of rhodium is between about 10 and about 70 atomic percent, and tin or copper is at a concentration that is between about 15 and about 70 atomic percent.

13. The catalyst of claim 1 wherein the concentration of platinum is between about 10 and about 60 atomic percent, the concentration of rhodium is between about 20 and about 60 atomic percent, and tin or copper is at a concentration that is between about 20 and about 60 atomic percent.

14. The catalyst of claim 1 wherein the concentration of platinum is between about 5 and about 70 atomic percent, the concentration of rhodium is between about 5 and about 70 atomic percent, tungsten is at a concentration that is between about 5 and about 70 atomic percent, and tin, molybdenum, or copper is at a concentration  
5 that is between about 5 and about 70 atomic percent.

15. The catalyst of claim 1 wherein the concentration of platinum is between about 10 and about 50 atomic percent, the concentration of rhodium is between about 10 and about 50 atomic percent, tungsten is at a concentration that is between about 10 and about 50 atomic percent, and tin, molybdenum, or copper is at a concentration that is between about 10 and about 50 atomic percent.

16. The catalyst of claim 1 wherein the concentration of platinum is between about 15 and about 25 atomic percent, the concentration of rhodium is between about 15 and about 25 atomic percent, tungsten is at a concentration that is between about 15 and about 45 atomic percent, and tin is at a concentration that is between about 15 and about 45 atomic percent.

17. The catalyst of claim 1 wherein the concentration of platinum is between about 15 and about 25 atomic percent, the concentration of rhodium is between about 15 and about 25 atomic percent, tungsten is at a concentration that is between about 15 and about 25 atomic percent, and molybdenum is at a concentration that is between about 35 and about 45 atomic percent.

18. The catalyst of claim 1 wherein the concentration of platinum is between about 15 and about 25 atomic percent, the concentration of rhodium is between about 15 and about 25 atomic percent, tungsten is at a concentration that is between about 25 and about 45 atomic percent, and copper is at a concentration that is between about 10 and about 40 atomic percent.

19. The catalyst of claim 1 wherein the concentration of platinum is between about 30 and about 50 atomic percent, the concentration of rhodium is between about 10 and about 30 atomic percent, copper is at a concentration that is between about 10 and about 30 atomic percent, and molybdenum is at a concentration that is between about 10 and about 30 atomic percent.

20. The catalyst of claim 1 wherein the concentration of platinum is between about 10 and about 30 atomic percent, the concentration of rhodium is between about 10 and about 50 atomic percent, tin is at a concentration that is between about 10 and about 30 atomic percent, and molybdenum is at a concentration that is between about 10 and about 50 atomic percent.

21. The catalyst of claim 1 wherein the concentration of platinum is between about 15 and about 25 atomic percent, the concentration of rhodium is between about 15 and about 25 atomic percent, tin is at a concentration that is between about 15 and about 25 atomic percent, and molybdenum is at a concentration that is  
5 between about 35 and about 45 atomic percent.

22. The catalyst of claim 1 wherein the concentration of platinum is between about 10 and about 25 atomic percent, the concentration of rhodium is between about 25 and about 40 atomic percent, tin is at a concentration that is between about 10 and about 25 atomic percent, and copper is at a concentration that is  
5 between about 25 and about 40 atomic percent.

23. The catalyst of claim 1 wherein the concentration of platinum is between about 10 and about 25 atomic percent, the concentration of rhodium is between about 10 and about 25 atomic percent, tungsten is at a concentration that is between about 10 and about 25 atomic percent, copper is at a concentration that is  
5 between about 25 and about 40 atomic percent, and molybdenum is at a concentration that is between about 10 and about 25 atomic percent.

24. The catalyst of claim 1 wherein the concentration of platinum is between about 10 and about 30 atomic percent, the concentration of rhodium is between about 10 and about 30 atomic percent, tin is at a concentration that is between about 10 and about 30 atomic percent, copper is at a concentration that is between  
5 about 20 and about 40 atomic percent, and molybdenum is at a concentration that is between about 10 and about 30 atomic percent.

25. The catalyst as in any one of claims 1-24 wherein the catalyst is an alloy comprising platinum, rhodium, at least one of tungsten, tin, and copper, and optionally molybdenum in metallic oxidation states, provided the platinum and rhodium are at concentrations such that the sum of said concentrations is no greater  
5 than 85 atomic percent.

26. A supported electrocatalyst powder for use in electrochemical reactor devices, the supported electrocatalyst powder comprising the catalyst as in any one

of claims 1-25 and electrically conductive support particles upon which the catalyst is dispersed.

27. The supported electrocatalyst powder of claim 26 wherein the electrically conductive support particles are selected from the group consisting of inorganic supports and organic supports.

28. The supported electrocatalyst powder of claim 27 wherein the electrically conductive support particles are selected from the group consisting of carbon supports and electrically conductive polymer supports.

29. A fuel cell electrode, the fuel cell electrode comprising electrocatalyst particles and an electrode substrate upon which the electrocatalyst particles are deposited, the electrocatalyst particles comprising the catalyst as in any one of claims 1-25.

30. The fuel cell electrode of claim 29 wherein the electrocatalyst particles comprise electrically conductive support particles upon which the catalyst is dispersed.

31. The fuel cell electrode of claim 30 wherein the electrically conductive support particles are selected from the group consisting of carbon supports and electrically conductive polymer supports.

32. A fuel cell comprising an anode, a cathode, a proton exchange membrane between the anode and the cathode, and the catalyst as in any one of claims 1-25 for the catalytic oxidation of a hydrogen-containing fuel or the catalytic reduction of oxygen.

33. The fuel cell of claim 32 wherein the fuel consists essentially of hydrogen.

34. The fuel cell of claim 32 wherein the fuel is a hydrocarbon-based fuel.

35. The fuel cell of claim 32 wherein the fuel comprises methanol.

36. The fuel cell of claim 32 wherein the catalyst is on the surface of the proton exchange membrane and in contact with the anode.

37. The fuel cell of claim 32 wherein the catalyst is on the surface of the anode and in contact with the proton exchange membrane.

38. The fuel cell of claim 32 wherein the catalyst is on the surface of the proton exchange membrane and in contact with the cathode.

39. The fuel cell of claim 32 wherein the catalyst is on the surface of the cathode and in contact with the proton exchange membrane.

40. A method for the electrochemical conversion of a hydrogen-containing fuel and oxygen to reaction products and electricity in a fuel cell comprising an anode, a cathode, a proton exchange membrane therebetween, the catalyst as in any one of claims 1-25, and an electrically conductive external circuit connecting the  
5 anode and cathode, the method comprising contacting the hydrogen-containing fuel or the oxygen and the catalyst to catalytically oxidize the hydrogen-containing fuel or catalytically reduce the oxygen.

41. The method of claim 40 wherein the hydrogen-containing fuel consists essentially of hydrogen.

42. The method of claim 40 wherein the hydrogen-containing fuel is a hydrocarbon-based fuel selected from the group consisting of saturated hydrocarbons, garbage off-gas, oxygenated hydrocarbons, fossil fuels, and mixtures thereof.

43. The method of claim 40 wherein the hydrogen-containing fuel is methanol.

44. An unsupported catalyst layer on a surface of an electrolyte membrane or an electrode, said unsupported catalyst layer comprising platinum, rhodium, at least one of tungsten, tin, and copper, and optionally molybdenum, in metallic

oxidation states, provided the platinum and rhodium are at concentrations such that  
5 the sum of said concentrations is no greater than 85 atomic percent.

1/2

FIG. 1

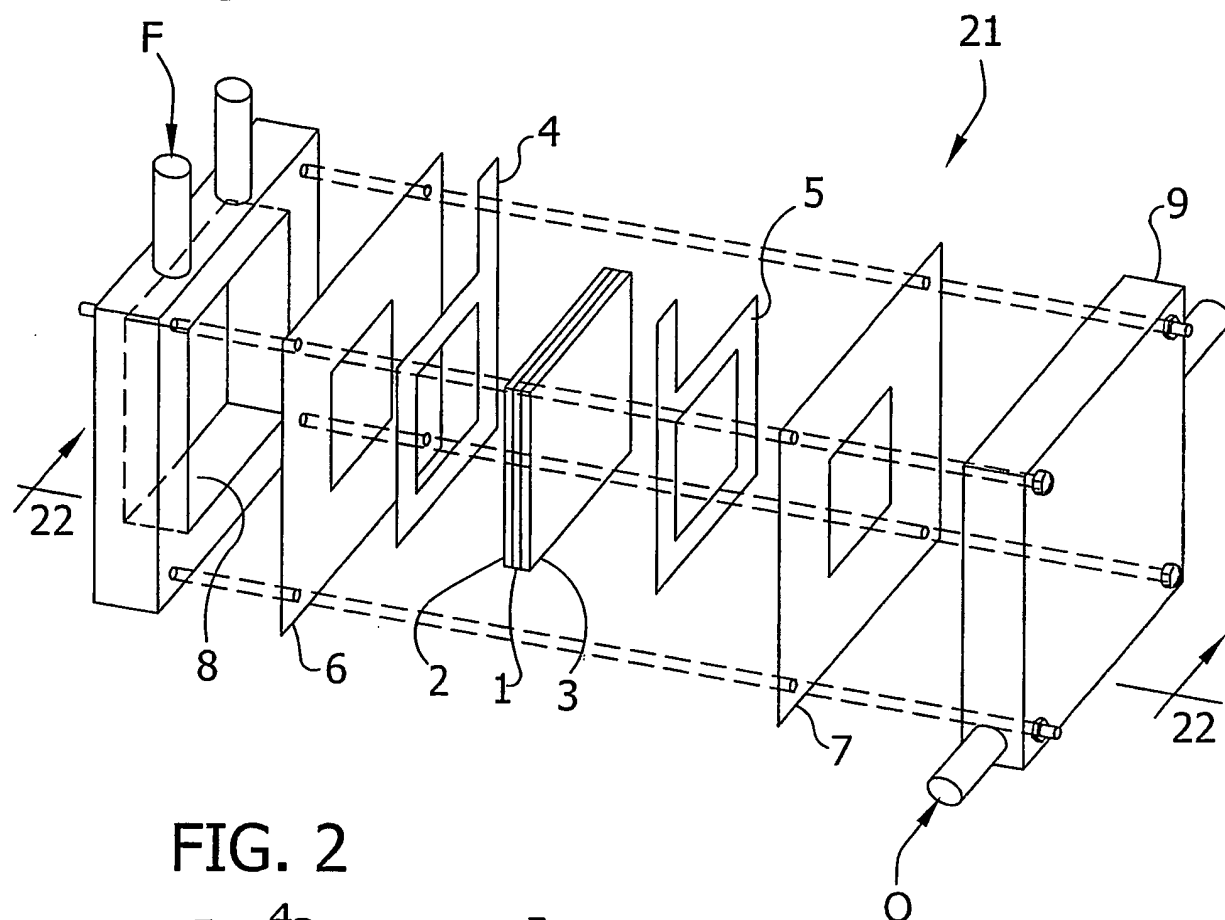
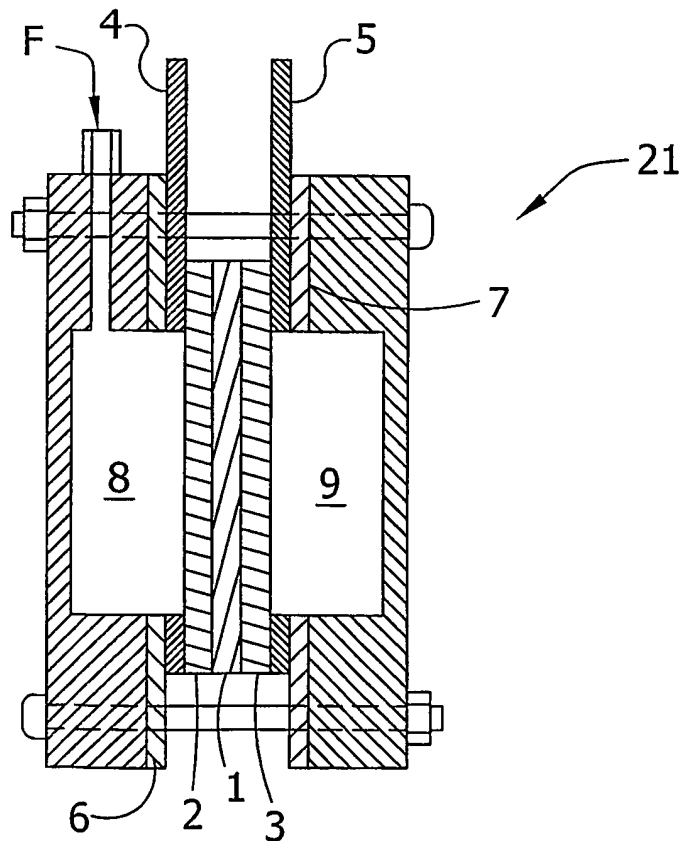
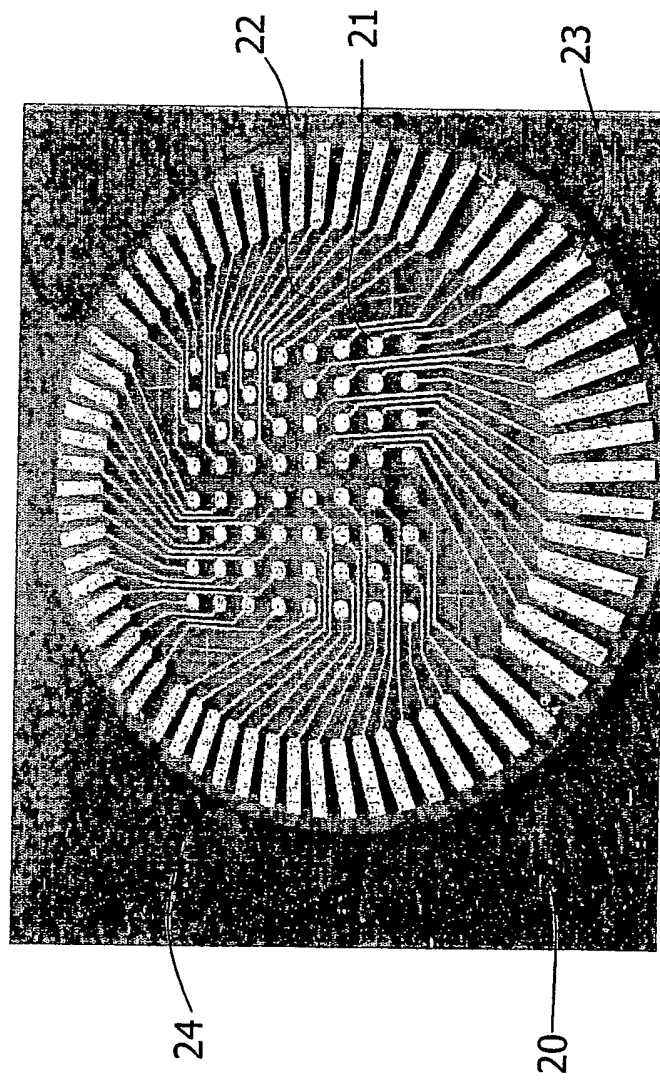


FIG. 2



2/2

FIG. 3





(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
2 October 2003 (02.10.2003)

PCT

(10) International Publication Number  
**WO 2003/081702 A3**

(51) International Patent Classification<sup>7</sup>: **H01M 4/92**,  
B01J 23/42, 23/46, 23/56, 23/652, 23/62, 23/72, 23/89,  
C22C 5/04

(21) International Application Number:  
PCT/US2003/008852

(22) International Filing Date: 21 March 2003 (21.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/366,519 21 March 2002 (21.03.2002) US

(71) Applicants (*for all designated States except US*): SYMYX  
TECHNOLOGIES, INC. [US/US]; 3100 Central Ex-  
pressway, Santa Clara, CA 95051 (US). HONDA GIKEN  
KOGYO KABUSHIKI KAISHA [JP/JP]; c/o Kabushiki  
Kaisha Honda, Gijyutsu Kenkyusho, 4-1, Chuo-1-chome,  
Wako-shi, Saitama 351-0193 (JP).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): STRASSER, Peter  
[DE/US]; 551 Mariposa Avenue, Apt. 7, Mountain View,  
CA 94041 (US). GORER, Alexander [IL/US]; 455 Mill  
River Lane, San Jose, CA 95134 (US). DEVENNEY,  
Martin [IE/US]; 1311 Bonita Avenue, Mountain View,  
CA 94040 (US). FAN, Qun [US/US]; 1178 Quintana  
Way, Fremont, CA 94539 (US). CHONDROUDIS,  
Konstantinos [GR/US]; 542 Firloch Avenue, Apt. #3,  
Sunnyvale, CA 94086 (US). GIAQUINTA, Daniel,  
M. [US/US]; 149 Jasmine Court, Mountain View, CA  
94043 (US). HE, Ting [CN/US]; 5794 Norn Street,  
Dublin, OH 43016 (US). OYANAGI, Hiroyuki [JP/JP];  
c/o Kabushiki Kaisha Honda, Gijyutsu Kenkyusho,  
4-1, Chuo-1-chome, Wako-shi, Saitama 351-0193 (JP).  
URATA, Kenta [JP/JP]; c/o Kabushiki Kaisha Honda,  
Gijyutsu Kenkyusho, 4-1, Chuo-1-chome, Wako-shi,

Saitama 351-0193 (JP). IWASAKI, Kazuhiko [JP/JP];  
c/o Kabushiki Kaisha Honda, Gijyutsu Kenkyusho,  
4-1, Chuo-1-chome, Wako-shi, Saitama 351-0193 (JP).  
FUKUDA, Hiroichi [JP/JP]; c/o Kabushiki Kaisha Honda,  
Gijyutsu Kenkyusho, 4-1, Chuo-1-chome, Wako-shi,  
Saitama 351-0193 (JP).

(74) Agents: RITCHEY, Steven, M. et al.; Senniger, Powers,  
Leavitt & Roedel, 1 Metropolitan Square, 16th Floor, St.  
Louis, MO 63102 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD,  
SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US,  
UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,  
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report
- before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments

(88) Date of publication of the international search report:  
8 January 2004

*For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.*

(54) Title: FUEL CELL CATALYST CONTAINING PT AND RH AND AT LEAST ONE OF W, SN AND CU AND OPTION-  
ALLY MO.

(57) Abstract: An improved fuel cell catalyst containing platinum, rhodium at least one of tungsten, tin, and copper, and optionally  
molybdenum, in metallic oxidation states. Additionally, the platinum and rhodium are at concentrations such that the sum of their  
concentrations is not greater than 85 atomic percent.

WO 2003/081702 A3

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 H01M4/92 B01J23/42 B01J23/46 B01J23/56 B01J23/652  
 B01J23/62 B01J23/72 B01J23/89 C22C5/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M B01J C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 364 072 A (AUSTIN BARBER WILLIAM) 16 January 1968 (1968-01-16)	1-6,14, 15,17, 29,44
Y	column 2, line 10 - line 15; example 2  column 2, line 37 - line 49 -----	26-28, 30-43
X	US 3 357 863 A (KENNETH ZIERING LANCE) 12 December 1967 (1967-12-12)	1-6,29, 44
Y	the whole document  -----	26-28, 30-43
Y	WO 00 35037 A (HOOGERS GREGOR ; JOHNSON MATTHEY PLC (GB); COOPER SUSAN JOY (GB)) 15 June 2000 (2000-06-15) examples 1-5; table 2 -----	26-28, 30-43
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

1 August 2003

Date of mailing of the international search report

31.10.03

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Hintermaier, F.

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 99 27590 A (CALIFORNIA INST OF TECHN) 3 June 1999 (1999-06-03) page 15 - page 21 -----	26-28, 30-43
X	US 4 401 557 A (JUGUIN BERNARD ET AL) 30 August 1983 (1983-08-30) abstract column 3, line 34 - line 63; table 1 -----	1-10

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-11, 14-18, 23, 25-44

**Remark on Protest**

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-11, 14-18, 23, 25-44

Catalyst composition comprising Pt, Rh and W in metallic oxidation states. Supported catalyst, unsupported catalyst layer, fuel cell electrode and fuel cell comprising said composition. Method for electrochemical conversion of a hydrogen-containing fuel and oxygen using a catalyst having said composition.

---

2. claims: 12,13,20-22,24

Catalyst comprising Pt, Rh and Sn in metallic oxidation states.

---

3. claim: 19

Catalyst comprising Pt, Rh and Cu in metallic oxidation states.

---

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3364072	A	16-01-1968	NONE	
-----				
US 3357863	A	12-12-1967	BE 692936 A	20-07-1967
			DE 1517988 A1	23-07-1970
			FR 1494653 A	08-09-1967
			GB 1144824 A	12-03-1969
			NL 6608305 A	24-07-1967
-----				
WO 0035037	A	15-06-2000	AT 220247 T	15-07-2002
			CA 2354133 A1	15-06-2000
			DE 69902058 D1	08-08-2002
			DE 69902058 T2	19-12-2002
			DK 1155465 T3	21-10-2002
			EP 1155465 A1	21-11-2001
			ES 2179689 T3	16-01-2003
			WO 0035037 A1	15-06-2000
			JP 2002532833 T	02-10-2002
-----				
WO 9927590	A	03-06-1999	AU 1996099 A	15-06-1999
			WO 9927590 A1	03-06-1999
			US 6291093 B1	18-09-2001
-----				
US 4401557	A	30-08-1983	FR 2286187 A1	23-04-1976
			BE 833584 A1	19-03-1976
			CA 1085372 A1	09-09-1980
			DE 2541186 A1	15-04-1976
			DK 429175 A	26-03-1976
			ES 441209 A1	01-07-1977
			GB 1511537 A	24-05-1978
			IN 140907 A1	01-01-1977
			IT 1042870 B	30-01-1980
			JP 1177207 C	14-11-1983
			JP 51057690 A	20-05-1976
			JP 58005701 B	01-02-1983
			NL 7511321 A	29-03-1976
			SE 7510649 A	26-03-1976
			ZA 7505839 A	25-08-1976
-----				

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☒ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**